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Abstract

In the three phase catalytic reactions or in floatation the position of particles in respect to the gas/liquid interface is a crucial parameter affecting the efficiency of those processes. It is commonly assumed that three phase interactions are described by the contact angle, and in general the higher the contact angle the greater the probability of the particle attachment to gas/liquid interface. Contact angles are notoriously difficult to measure accurately for porous particles of wide size distribution and/or irregular shape. Also, it is practically impossible to measure the contact angles at high temperature/pressure e.g. at the conditions typical in many catalytical reactors.

Here new method, based on thermodynamical description of the interfacial/surface energies, enabling prediction of the position of particles in a three phase solid/gas/liquid systems is discussed. In this method the surface energy of catalyst particles at elevated temperatures is measured using inverse gas chromatography enabling calculation of total interaction energy between three phases and the prediction of the position of particles in

gas/liquid dispersion. The predictions were in very good agreement with experimental results obtained with the bubble pick up method.

1. Introduction

The position of solid particles in respect to fluid/liquid interface might critically affect efficiency of flotation processes (Ralston *et al.* 1999; Albijanic *et al.* 2010; Muganda *et al.* 2011), stability of emulsion (Pickering 1907; Binks 2002; Binks *et al.* 2005) as well as overall reaction rate in multiphase catalitical reactors (Vinke *et al.* 1991; Ruthiya *et al.* 2004; Junmei *et al.* 2006; Hu *et al.* 2007). Prediction of the position of the solid particles in gas/solid/liquid systems (in the bulk of liquid or at the interface between two gas and liquid) is rather difficult and the simple method based on the values of contact angle is not always accurate. According to this method it is commonly accepted that in gas/liquid/solid dispersions, the particles might stay on the gas/liquid interface when the three phase contact angle $\theta > 0°$ (Vinke *et al.* 1991; Dai *et al.* 1999) and the larger the contact angle the stronger the attachment. Whilst indication of the position of particles based on the value of the contact angle is simple and straightforward the measurements of contact angle between particle and liquids as such might be challenging (Nowak et al. 2013; Nowak et al. 2013a) Even at the room temperature/pressure such measurements for porous particles (catalyst) is not straightforward and it is practically impossible to obtain accurate values of contact angles at the elevated temperature/pressure typical for many multiphase catalitical reactors. The contact angles measured at room temperature might be different than contact angle at

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elevated temperature since the surface tension and surface/interfacial energy depends on the temperature (Israelachvili 2011).

In this work, the position of solid particles in gas/solid/oil dispersions has been investigated theoretically and experimentally. The theoretical considerations are based on thermodynamical description of the work of adhesion/cohesion (Israelachvili 2011) applied to macroscopic system. This methodology enables prediction of the particles most favourable position, i.e. whether they tend to remain in the bulk of the liquid or at the gas/liquid interface.

The work associated with the particle detachment from the gas/liquid interface can be expressed in terms of surface energies between: gas/solid (γ_{sg}), gas/liquid (γ_{lg}) and solid/liquid (γ_{sl}) as ilustrated in Figure 1.

The energy of the particle detachment (ΔE) can be expressed in terms of work of adhesion between solid/liquid and gas/solid ($W_a = \gamma_{lg} + \gamma_{sg} - \gamma_{sl}$) and work of the liquid cohesion ($W_c = 2\gamma_{lg}$) (Israelachvili 2011):

$$\Delta E = W_c - W_a = \gamma_{lg} + \gamma_{sl} - \gamma_{sg} \tag{1}$$

For the $\Delta E > 0$, $\gamma_{lg} + \gamma_{sl} > \gamma_{sg}$ the attraction between gas and solid is stronger than attraction between liquid and solid, therefore the particle tent to adhere/attach to gas/liquid interface. For the $\Delta E < 0$, $\gamma_{lg} + \gamma_{sl} < \gamma_{sg}$ liquid displaces gas on the solid surface and totally wets the solid therefore the particles tend to stay in the liquid. Therefore, if the surface energies between gas/liquid (γ_{lg}), gas/solid (γ_{sg}) and solid liquid (γ_{sl}) are known it is possible to predict the position of particles in gas/liquid dispersion. Whilst the energy

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between gas and pure liquids (surface tension, γ_{lg}) is readily available in the tables of physical properties (Yaws 2012) the gas/solids surface energies (γ_{sg}) and solid/liquid interfacial energy (γ_{sl}) strongly depend on the treatment of the solid surfaces (Schmidt 2001) therefore are not available in the literature and they have to be measured.

The interfacial energy between solid and liquid consists of their surface energies reduced by the energy of interactions between them due to polar and non-polar (dispersive) forces (Fowkes 1962; Fowkes 1987). Depending on the physical properties of solid and liquid (polarity, dielectric constant etc.) the interactions can be either entirely due to the dispersive forces or it can also have the polar components (Van Oss *et al.* 1988) (Fowkes 1987):

$$\gamma_{sl} = \gamma_{sg} + \gamma_{lg} - 2\left(\gamma_{sg}{}^{d} \cdot \gamma_{lg}{}^{d}\right)^{1/2} - 2\left(\gamma_{sg}{}^{p} \cdot \gamma_{lg}{}^{p}\right)^{1/2} \tag{2}$$

The systems investigated here consist of non-polar oil, therefore interactions with catalysts particles can occur only due to dispersive forces. In such case the interaction energy can be calculated from (Fowkes 1962; Fowkes 1964):

$$\gamma_{sl} = \gamma_{sg} + \gamma_{lg} - 2\left(\gamma_{sg}{}^{d} \cdot \gamma_{lg}{}^{d}\right)^{1/2} \tag{3}$$

and the change of system energy from:

$$\Delta E = 2\gamma_{lg} - 2\left(\gamma_{sg}{}^{d} \cdot \gamma_{lg}{}^{d}\right)^{1/2} \tag{4}$$

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This means that the energy of the particle attached to the bubble can be determined if the dispersive component of surface free energy of the article is known as dispersive component of gas/liquid interaction are equal to the surface tension of the non-polar oil.

Interfacial energy between solid and gas strongly depends on the processing methods, e.g. solids processed at low temperature have different surface energy than the same solid processed at high temperature; also chemical treatment affects surface energy as it might change the zeta potential (Schmidt 2001).

Recently inverse gas chromatography (IGC) has been employed to measure dispersive component of surface energy of both porous and non-porous solid particles (Diaz *et al.* 2007; Xue *et al.* 2008; Cuervo *et al.* 2009; Das *et al.* 2010; Grajek *et al.* 2010; Shi *et al.* 2011; Kolodziejek *et al.* 2013). In inverse gas chromatography net retention volume/time depends on the strength of the interactions between fluid (probes) and adsorbent (solids) (Xie *et al.* 2000):

$$V_N = jF\left(t_r - t_0\right)CT \tag{5}$$

The retention volume is related to the adsorption energy of the solid phase (Liu *et al.* 1998; Grajek *et al.* 2010):

$$\Delta G_{ads} = -RT\ln V_N + const \tag{6}$$

where the constant depends on the type of chromatographic column and selected reference state.

The adsorption of probe molecules is caused by dispersive and polar interactions and can be related to the work of adhesion by (Grajek *et al.* 2010):

$$\Delta G_{ads} = -N_A a W_{adh} \tag{7}$$

where *a* is a molecular area of an adsorbed molecule (Diaz *et al.* 2005):

$$a = 1.09 \cdot 10^{14} \left(\frac{M}{\rho N_A} \right)^{2/3} \tag{8}$$

The relation between the adsorption energy and the work of adhesion enables calculation of the surface energy of solid particles from measured retention volume. Because non-polar liquids adsorption can occur only due to dispersive forces the dispersive component of the particles surface energy can be obtained from (Newell *et al.* 2001):

$$RT \ln V_N = 2N_A \left(y_s^d \right)^{1/2} a \left(\gamma_l^d \right)^{1/2} + const \tag{9}$$

and it is equal to the slope of the line defined by Eq 9 in ($RT\ln V_n$) versus (($\gamma_1^d)^{1/2}$) coordinates. This means that when the particles surface energy in presence of a the non-polar liquid is known the position of catalyst particles in gas/solid/oil systems can be predicted. It is worth to stress here that this approach enables calculation of surface energy at an elevated temperature/pressure e.g. conditions frequently occurring in the industrial applications.

 In this work inverse gas chromatography was used to measure surface energy of selected catalyst particles at elevated temperatures. The results were compared with the predictions

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based on the values of contact angle (Nowak *et al.* 2013) and validated against experimental results obtained with the bubble pick up method (Vinke *et al.* 1991).

2. Experimental

Two sets of experiments were carried out.

In the first set the dispersive components of the surface energy of catalyst particles in (i) the set of consecutive alkanes of monotonically increasing molecular size and (ii) in the non-polar viscous (vara oil) and non-viscous (n-decane) liquids were measured. The measurements carried out with alkanes were aimed at verification of the theoretical method used for prediction of the position of particles in gas/solid/liquid suspensions discussed above. The measured dispersive component of surface energy of the particles with paraffin oil and with n-decane were used to predict the position of particles in such systems and to compare the results with the prediction based on the values of the contact angle (Nowak 2013).

In the second set of experiments the attachment of the catalyst particles to a single bubble suspended in the paraffin oil and in the n-decane was investigated and the results were compared with the theoretical predictions based on the dispersive components of surface energy and on the contact angle.

2.1. Materials

The following catalyst supports supplied by Johnson Matthey were investigated: Al_2O_3 (d_{32}=16µm), SiO_2 (d_{32}=13µm), ZrO2 (d_{32}=26µm) and details of all physical properties can be found elsewhere (Nowak *et al.* 2013). Supplied by Johnson Matthey viscous oil (Heavy Liquid Paraffin VARA 600/240 PB, CAS No: 8042-47-5; EINECS No: 2324558) fulfil the DAB/BP/USP and FDA regulation 21 CFR 178.3570 on the purity requirements. Range of

alkanes (C_6H_{14}, C_7H_{16}, C_8H_{18}, C_9H_{20} and $C_{10}H_{22}$) was purchased from Sigma-Aldrich. The properties of liquids used are lited in Table 1.

2.2. <u>Inverse gas chromatography</u>

The inverse gas chromatography involves injection of fluid (vapour) into a column filled with the investigated particles and measurements of the retention time as in the standard chromatography. However in this case rather than composition of the liquid phase (standard chromatography) the strength of interaction between fluid (adsorbate) and solid (adsorbent) is determined from the measured retention time. IGC can be used to measure range of physical properties such as adsorption isotherms, heats of adsorption, solubility coefficients, free energy of adsorption, as well as, polar and dispersive components of surface free energy (Newell *et al.* 2001; Diaz *et al.* 2005; Xue *et al.* 2008; Das *et al.* 2010). This method is frequently used to characterise powder surface properties in pharmaceutical industry (Grimsey *et al.* 2002), coatings (Hegedus *et al.* 1993), composite particles (York *et al.* 1998) and also to characterise surface properties of catalysts (Diaz *et al.* 2005; Cuervo *et al.* 2009).

In this work gas chromatograph Perkin-Elmer 8500 equipped with the flame ionization detector and copper column (length of 30cm and inner diameter of 2mm) enabling measurements at high temperature and pressure was used. The column was filled with investigated particles using vacuum pump, silanized wool stoppers were inserted at the both ends and column was left for 24h at 100°C with inert gas (nitrogen) passing through it in order to remove all impurities and water vapour. The temperature of the injection port was set above the boiling point of all investigated liquids (230°C) to ensure complete evaporation of injected liquids. During the experiments gas flow rates were measured using bubble in water flow-meter. Each measurement was repeated 3 times for each liquid/solid combination and

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the average retention time was used to calculate retention volume. The dispersive component of solid surface energies was determine using following alkanes C_6H_{14}, C_7H_{16}, C_8H_{18}, C_9H_{20} . In order to stay within linear regime of adsorbtion, the vapours were strongly diluted in nitrogen (1 µl Hamilton syringe) before the mixture was injected into the column. At the infinite dilution the adsorbate covers small fraction of the adsorbent and the results are not affected by adsorbate-adsorbate interactions (Mukhopadhyay *et al.* 1995). The time of passing non-adsorbing fluid (dead time) was measured using methane also at very low concentration. Table 2 summarizes experimental conditions.

2.3. Particles to a single bubble attachment

The attachment of the particles submersed in liquid to the single bubble was investigated in an experimental rig schematically shown in Figure 2.

Particles (1) were suspended in the liquid in a glass, rectangular container (4) placed on the stand (6) enabling vertical movement and were left to sediment for 24 hours. After that time the air bubble (3) was formed at the tip of the syringe needle of 1.81 mm diameter (5) immersed in the oil and the container was slowly moved towards the gas bubble until the bubble was completely immersed in the particles. Next the bubble was withdrawn from the bed of particles by slowly lowering the stand and the coverage of bubble with particles was estimated directly from high resolution images of bubbles with attached particles taken by video-technique (7) (Pacek *et al.* 1994). The three phase contact angles between particles, gas and oil were calculated from the degree of coverage of the bubble surface by the particles.

3. Results and discussion

3.1. Dispersive component of particles surface energy measured using alkanes

Molar free energies of adsorption ($RT\ln V_n$) of set of alkanes on alumina, silica and zirconia catalyst calculated from net retention volumes measured at different temperatures are summarised in Figure 3. There is a nearly perfect linear relation between the product of alkane molecular area and square root of surface tension and energy of adsorption at all investigated temperature as theoretically predicted by the combination of Eq 6 and 9 (Rodriguez *et al.* 1997; Liu *et al.* 1998). As expected, the higher the molecular weight of alkanes the larger the energy of adsorption and the longer the retention time. The free energy of adsorption of the consecutive alkanes increased with the molecule size, i.e. in the investigated case the dispersive forces between particles and non-polar liquids increases with number of alkyl groups ($-CH_3$). This and the fact in all investigated systems the energy of adsorption decreases with temperature indicate that the results are consistent.

Dispersive components of surface free energy (γ_l^d) were calculated, based on the equation 9, from the slope of the best fit lines in Figure 3 and are summarised in Figure 4.

Higher dispersive component of the surface energy of the particles compared to paraffin oil and n-decane surface tension (Table 1) indicate that liquid will tend to spread completely over the solid surface (energetically more favourable position). This means that in the three phase system (air/non-polar liquid/particles) at ambient conditions the particles will tend to remain in the bulk of liquid.

Figure 4 shows that the dispersive component of surface energy linearly decreases with temperature what agrees with the results reported in the literature for Pd/Al$_2$O$_3$ (Diaz *et al.* 2004), Pd/SDB catalysts (Xie *et al.* 2000) and activated carbons (Diaz *et al.* 2005). Since

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surface tension of the liquids decreases linearly with temperature, therefore measured surface energies of solid were approximated by linear correlation (Israelachvili 2011).

In general there is good agreement between the values of the surface free energy reported in literature and the results shown in Figure 4. Diaz et al. (2004) reported surface free energy of γ-Al$_2$O$_3$ measured by inverse gas chromatography of 59.3 mJ/m^2 at 200°C whereas this studies gives 25.3 mJ/m^2 for alumina at this temperature. The dispersive parts of surface free energies of crystalline silica and fused silica reported in literature are 31.78 mJ/m^2 and 37.81 mJ/m^2 at 140°C respectively (Yang and Yoon 2007) are close to 24.8 mJ/m^2 measured here. Considering that the dispersive part of the surface free energy of particles strongly depends on the method of production and thermal treatment the values obtained in this work seem to be in a good agreement with the literature data.

3.2. Particles in three phase system

Calculated dispersive component of the particles surface energy allows estimation of the position of the particles in gas/non-polar liquids (e.g in low dielectric constant hydrocarbons) system based on thermodynamical equilibrium. System net change of energy upon particles detachment from the gas/liquid interface to bulk of the liquid (based on Eq. 1) was calculated for each catalyst particles for non-polar liquids, decane and paraffin oil. Results were extrapolated to 25°C (Figure 5).

The more positive the net change of energy, the more energetically favourable the presence of the particles in the bulk of the liquid. Negative values mean that the position of the particles on the interface is energetically favourable.

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In the paraffin oil, at all temperatures, silica particles revealed the lowest net change of energy (ΔE). This means that these particles are likely to stay on the interface. Interestingly, in the Fisher Tropsch synthesis conditions (T $=210^{0}$C), the net change of energy with the silica particles is negative, what indicates that silica catalyst particles tend to attach to the surface of the bubble. It is impossible to predict the position of catalyst particles under such processing conditions based on the values of the contact angle alone. Clearly these particles show smallest attraction to the paraffin oil what is also consistent with the lowest dispersive part of surface energy as compared to zirconia and alumina. It can be therefore concluded that also at room temperature, interaction of silica particles with oil is weakest what results in the largest work of particle attachment. Silica particles suspended in decane would not show strong attachment to the air/decane interface.

Calculated energy of the particles detachment from the bubble surface to the bulk of liquid is always positive for alumina and zirconia particles (Figure 5a). This indicates that both these particles are expected to stay suspended in the bulk of liquid rather than at the liquid/gas interface. Changes of the energy for the zirconia particles is largest, therefore these particles are most likely to remain in the bulk of the liquid.

3.3 Position of particles in the single bubble/non-polar liquid system

The particles attachment to the bubble suspended in high and low viscosity non-polar liquids was investigated following methodology described in the section 2. Figure 6 shows typical images of the particles and bubble in the paraffin oil (6a) and in the n-decane (6b).

The experiments clearly show that some particles remain at the air-paraffin oil or air-decane interface what indicate certain degree of particles lyophobicity. This is rather unexpected when the contact angle values are considered. Previously published measurements of the contact angle between particles and paraffin oil showed that particles

are lyophilic, i.e. zero contact angle was obtained for all particles (Al_2O_3, SiO_2 and ZrO_2) (Nowak *et al.* 2013). These results suggest that the particles tend to stay in the bulk of the non-polar liquid rather than at the gas/liquid interface. Based on the contact angles values one would expect complete wetting what is observed here as it can be clearly seen in Figure 6 that some particles remain attached to the bubble. Such contradiction proves that the prediction of the particle position in gas/soild/liquid system based only on the values of contact angles might lead to wrong conclusions. Figure 6a clearly shows that there is certain amount of the silica particles attached to the bubble as well as several alumina particles. In decane, few silica particles were visible at the gas/liquid interface. Zirconia was not present at the gas/liquid interface neither in the paraffin oil nor in the decane.

The above images agree well with the results shown in Figure 5 representing the trends in the degree of particles wettability. It appears that silica is the least wettable by the paraffin oil (and decane) with even negative ΔE at different temperatures. The alumina particles are slightly better wetted but the zirconia particles are clearly the most wettable particles. These trends agree well with the observed amounts of different particles attached to gas bubble in non-polar liquids investigated here.

In general, for the negative values of ΔE attachment of the particles to the bubble surface is more favourable than suspension in the bulk of the liquid. At ambient temperatures, ΔE for silica particles in paraffin oil is positive, however is close to the zero (Figure 5a)). In the image however there is significant amount of particles attached to gas/liquid interface (Figure 6a). Also, few silica particles attached to the surface in air/decane system is unexpected since in this system ΔE is positive. Alumina particles have moderately positive ΔE in paraffin oil but still the minute attachment was observed (compare Figure 5a and 6a). No particles are present at the air/decane interface what agrees with the positive values

calculated for this system. Zirconia particles had the largest positive values of ΔE what is with very good agreement with observed complete absence of particles at either air/paraffin oil or air/decane interface (Figure 6).

Though the general trends in the ΔE values for all investigated systems are in a good agreement with the observed particles attachment, the absolute values of ΔE are less consistent. There might be two reasons for this. For each system, ΔE was calculated based on the dispersive component of the surface energy obtained from the linear extrapolation of the results obtained at 100-210°C to room temperature which might already carry certain error. More important however is the procedure used to test the particles attachment to bubble. Bubble is practically pushed into the particles bed (see Figure 2) therefore additional force is exerted on the particles-bubble interface. The particle to the bubble attachment results mostly from the capillary force, which is proportional to the circumference of the part of particle protruding into bubble ($2\pi R_p$) (van der Zon *et al.* 2002; Omota *et al.* 2006). During the particle attachment experiment, bubble is pushed into the particles bed what might increase penetration of particle into bubble, therefore larger circumference, hence larger capillary force. Such additional 'pushing' force might be especially important when particles are porous. The liquid might drain from the pores at the time the bubble is pushed into the particles bed increasing the tendency of particle to remain attached to the bubble. Therefore at room temperature, the data should be considered as trends rather than absolute values.

Using the Young definition of the contact angle and the expression for the energy change, the contact angle can be calculated at high temperatures. From the following relation (for the non-polar liquid)

$$\Delta E = 2\gamma_{lg} - 2\left(\gamma_{sg}{}^{d} \cdot \gamma_{lg}{}^{d}\right)^{1/2} = \gamma_{lg}\left(1 - \cos\theta\right) \tag{10}$$

contact angles between silica and paraffin oil can be calculated and are 23° and 33° at 170°C

and 210°C respectively.

4. Conclusions

This paper presents method of predicting the position of fine catalyst particles in

gas/oil system at s at elevated temperatures. Since the wettability of particles with paraffin

oil (or decane) cannot be reliably described by the contact angle, another approach, based

purely on the interfacial energies of the considered system is proposed here. This approach

identifies differences in interactions between different particles and liquid.

Work/energy of particles attachment to bubble suspended oil is employed as a key

parameters and it replaces the contact angle commonly used to assess the position of

particles. Direct measurements of particles to bubble attachment prove that the proposed here

method works and that contact angles cannot be use to predict the attachment.

Zirconia particles has the largest dispersive component of the surface energy,

therefore its interaction with non-polar oil is the strongest what indicate zirconia particles

suspended in non-polar oil/gas dispersion should tend to stay in the bulk of liquid. On the

other hand dispersive interactions between silica and non-polar oil is the weakest what

implies that non-polar oil will not tend to spread on silica surface and silica particles suspend

in gas/oil dispersion will tend to stay at the interface.

Nomenclature

a the cross-sectional area of the probe defined in Eq. 8, m^2

C corrective pressure in Eq. 5, $C = 1 - \dfrac{P_{H_2O}}{P_{out}}$

ΔE change of the three phase system energy upon particles detachment from gas/liquid

   interface as defined in Figure 1, J/m^2

F volumetric flow rate in Eq. 5, m^3/s

G_{ads} adsorption energy (in Eq. 6, 7), J

j James-Martin factor for the correction of gas compressibility under pressure difference,

$$j = \frac{2}{3} \frac{\left[\dfrac{P_{in}}{P_{out}} \right]^2 - 1}{\left[\dfrac{P_{in}}{P_{out}} \right]^3 - 1}$$

   in Eq. 5

M molar weight of the solute, g/mol

N_A Avogadro constant, $6.02 \cdot 10^{23}$ mol^{-1}

R universal gas constant, 8.314 J/mol K

t_r retention time, s

t_0 dead time, measured with methane, s

T column temperature, K

V_N retention volume, m^3/g

$W_{a,c}$ work of adhesion and cohesion as defined in text, J/m^2

Greek symbols

γ_{lg} gas/liquid surface energy, J/m^2

γ_{sg} gas/solid surface energy, J/m^2

γ_{sl} soli/liquid surface energy, J/m^2

γ_l^d dispersive component of liquid surface tension, J/m^2

γ_s^d dispersive component of solid surface energy, J/m^2

γ_l liquid surface tension, J/m^2

ρ liquid density, kg/m^3

θ three phase contact angle, deg

References

Albijanic, B., O. Ozdemir, A. V. Nguyen and D. Bradshaw (2010). "A review of induction
and attachment times of wetting thin films between air bubbles and particles and its
relevance in the separation of particles by flotation." Advances in Colloid and
Interface Science **159**(1): 1-21.

Binks, B. P. (2002). "Particles as surfactants—similarities and differences." Current Opinion
in Colloid & Interface Science **7**(1–2): 21-41.

Binks, B. P. and C. P. Whitby (2005). "Nanoparticle silica-stabilised oil-in-water emulsions:
improving emulsion stability." Colloids and Surfaces a-Physicochemical and
Engineering Aspects **253**(1-3): 105-115.

Cuervo, M. R., E. Díaz, B. de Rivas, R. López-Fonseca, S. Ordóñez and J. I. Gutiérrez-Ortiz
(2009). "Inverse gas chromatography as a technique for the characterization of the
performance of Mn/Zr mixed oxides as combustion catalysts." Journal of
Chromatography A **1216**(45): 7873-7881.

Dai, Z. F., D. Fornasiero and J. Ralston (1999). "Particle-bubble attachment in mineral
flotation." Journal of Colloid and Interface Science **217**(1): 70-76.

Das, S. C., I. Larson, D. A. V. Morton and P. J. Stewart (2010). "Determination of the Polar and Total Surface Energy Distributions of Particulates by Inverse Gas Chromatography." Langmuir **27**(2): 521-523.

Diaz, E., S. Ordonez and A. Vega (2007). "Adsorption of volatile organic compounds onto carbon nanotubes, carbon nanofibers, and high-surface-area graphites." Journal of Colloid and Interface Science **305**(1): 7-16.

Diaz, E., S. Ordonez, A. Vega and J. Coca (2004). "Adsorption characterisation of different volatile organic compounds over alumina, zeolites and activated carbon using inverse gas chromatography." Journal of Chromatography A **1049**(1-2): 139-146.

Diaz, E., S. Ordonez, A. Vega and J. Coca (2004). "Adsorption properties of a Pd/gamma-Al2O3 catalyst using inverse gas chromatography." Microporous and Mesoporous Materials **70**(1-3): 109-118.

Diaz, E., S. Ordonez, A. Vega and J. Coca (2005). "Comparison of adsorption properties of a chemically activated and a steam-activated carbon, using inverse gas chromatography." Microporous and Mesoporous Materials **82**(1-2): 173-181.

Diaz, E., S. Ordonez, A. Vega and J. Coca (2005). "Influence of catalyst treatments on the adsorption properties of gamma-Al2O3 supported Pt, Rh and Ru catalysts." Microporous and Mesoporous Materials **77**(2-3): 245-255.

Fowkes, F. M. (1962). "Determination of interfacial tensions, contact angles, and disperion forces in surfaces by assuming additivity of intermolecular interactions in surfaces." The Journal of Physical Chemistry **66**(2): 382-382.

Fowkes, F. M. (1964). "Attractive forces at interfaces." Industrial & Engineering Chemistry **56**(12): 40-52.

Fowkes, F. M. (1987). "Role of acid-base interfacial bonding in adhesion." Journal of Adhesion Science and Technology **1**(1): 7-27.

Grajek, H., J. Paciura-Zadrozna and Z. Witkiewicz (2010). "Chromatographic characterisation of ordered mesoporous silicas Part I. Surface free energy of adsorption." Journal of Chromatography A **1217**(18): 3105-3115.

Grimsey, I. M., J. C. Feeley and P. York (2002). "Analysis of the surface energy of pharmaceutical powders by inverse gas chromatography." Journal of Pharmaceutical Sciences **91**(2): 571-583.

Hegedus, C. R. and I. L. Kamel (1993). A review of inverse gas chromatography theory used in the thermodynamic analysis of pigment and polymer surfaces. Blue Bell, PA, ETATS-UNIS, Federation of Societies for Coatings Technology.

Hu, B., A. W. Nienow, E. H. Stitt and A. W. Pacek (2007). "Bubble Sizes in Agitated Water–Hydrophilic Organic Solvents for Heterogeneous Catalytic Reactions." Industrial & Engineering Chemistry Research **46**(13): 4451-4458.

Israelachvili, J. N. (2011). Intermolecular and Surface Forces, Third Edition, Academic Press.

Junmei, Z., X. Chunjian and Z. Ming (2006). "The mechanism model of gas-liquid mass transfer enhancement by fine catalyst particles." Chemical Engineering Journal **120**(3): 149-156.

Kolodziejek, J., E. Glowka, K. Hyla, A. Voelkel, J. Lulek and K. Milczewska (2013). "Relationship between surface properties determined by inverse gas chromatography and ibuprofen release from hybrid materials based on fumed silica." International Journal of Pharmaceutics **441**(1-2): 441-448.

Liu, F. P., T. G. Rials and J. Simonsen (1998). "Relationship of Wood Surface Energy to Surface Composition." Langmuir **14**(2): 536-541.

Muganda, S., M. Zanin and S. R. Grano (2011). "Influence of particle size and contact angle on the flotation of chalcopyrite in a laboratory batch flotation cell." International Journal of Mineral Processing **98**(3-4): 150-162.

Mukhopadhyay, P. and H. P. Schreiber (1995). "Aspects of acid-base interactions and use of inverse gas chromatography." Colloids and Surfaces A: Physicochemical and Engineering Aspects **100**: 47-71.

Newell, H. E., G. Buckton, D. A. Butler, F. Thielmann and D. R. Williams (2001). "The use of inverse phase gas chromatography to measure the surface energy of crystalline, amorphous, and recently milled lactose." Pharm Res **18**(5): 662-666.

Nowak, E. (2013). Bubbles – catalysts – oil interactions at elevated temperature and pressure in Fischer Tropsch synthesis.

Nowak, E., G. Combes, E. H. Stitt and A. W. Pacek (2013). "A comparison of contact angle measurement techniques applied to highly porous catalyst supports." Powder Technology **233**(0): 52-64.

Nowak, E., P. Robbins, G. Combes, E. H. Stitt and A. W. Pacek (2013a). "Measurements of contact angle between fine, non-porous particles with varying hydrophobicity and water and non-polar liquids of different viscosities." Powder Technology **250**: 21-32.

Omota, F., A. C. Dimian and A. Bliek (2006). "Adhesion of solid particles to gas bubbles. Part 1: Modelling." Chemical Engineering Science **61**(2): 823-834.

Pacek, A. W., I. P. T. Moore, A. W. Nienow and R. V. Calabrese (1994). "Video technique for measuring dynamics of liquid-liquid dispersion during phase inversion." Aiche Journal **40**(12): 1940-1949.

Pickering, S. U. (1907). "Emulsions." Journal of the Chemical Society, Transactions **91**: 2001-2021.

Ralston, J., D. Fornasiero and R. Hayes (1999). "Bubble–particle attachment and detachment in flotation." International Journal of Mineral Processing **56**(1–4): 133-164.

Rodriguez, M. A., J. F. Rubio, M. J. Liso and J. L. Oteo (1997). Application of inverse gas chromatography to the study of the surface properties of slates. Chantilly, Clay Minerals Society.

Ruthiya, K. C., J. van der Schaaf, B. F. M. Kuster and J. C. Schouten (2004). "Modeling the effect of particle-to-bubble adhesion on mass transport and reaction rate in a stirred slurry reactor: influence of catalyst support." Chemical Engineering Science **59**(22-23): 5551-5558.

Schmidt, H. (2001). "Nanoparticles by chemical synthesis, processing to materials and innovative applications." Applied Organometallic Chemistry **15**(5): 331-343.

Shi, B. L., Y. E. Wang and L. N. Jia (2011). "Comparison of Dorris-Gray and Schultz methods for the calculation of surface dispersive free energy by inverse gas chromatography." Journal of Chromatography A **1218**(6): 860-862.

van der Zon, A., P. J. Hamersma, E. K. Poels and A. Bliek (2002). "Coalescence of freely moving bubbles in water by the action of suspended hydrophobic particles." Chemical Engineering Science **57**(22-23): 4845-4853.

Van Oss, C. J., R. J. Good and M. K. Chaudhury (1988). "Additive and nonadditive surface tension components and the interpretation of contact angles." Langmuir **4**(4): 884-891.

Vinke, H., G. Bierman, P. J. Hamersma and J. M. H. Fortuin (1991). "Adhesion of small catalyst particles to gas bubbles: determination of small effective solid—liquid—gas contact angles." Chemical Engineering Science **46**(10): 2497-2506.

Vinke, H., P. J. Hamersma and J. M. H. Fortuin (1991). "Particle-to-bubble adhesion in gas/liquid/solid slurries." Aiche Journal **37**(12): 1801-1809.

Xie, J., Q. Zhang and K. T. Chuang (2000). "An IGC Study of Pd/SDB Catalysts for Partial Oxidation of Propylene to Acrylic Acid." Journal of Catalysis **191**(1): 86-92.

Xue, J. and Z. Zhang (2008). "Preparation and characterization of calcium-shellac spheres as a carrier of carbamide peroxide." Journal of Microencapsulation **25**(8): 523-530.

Yaws, C. L. (2003). Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds, Knovel.

Yaws, C. L. (2012). Yaws' Critical Property Data for Chemical Engineers and Chemists, Knovel.

York, P., M. D. Ticehurst, J. C. Osborn, R. J. Roberts and R. C. Rowe (1998). "Characterisation of the surface energetics of milled dl-propranolol hydrochloride using inverse gas chromatography and molecular modelling." International Journal of Pharmaceutics **174**(1–2): 179-186.
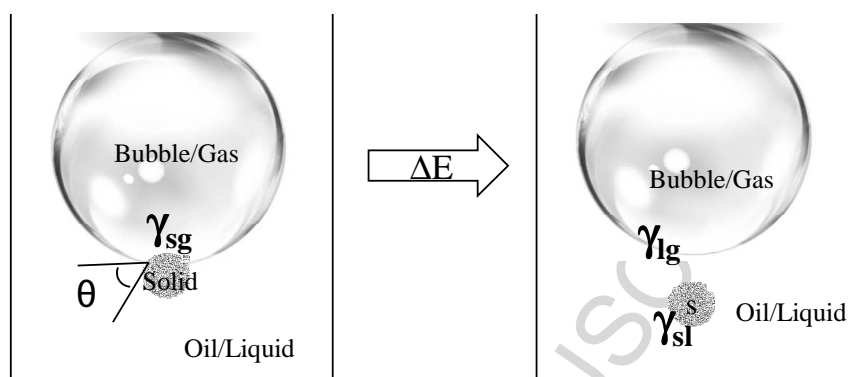
Figure 1. Energy associated with particles detachment from the gas/liquid interface
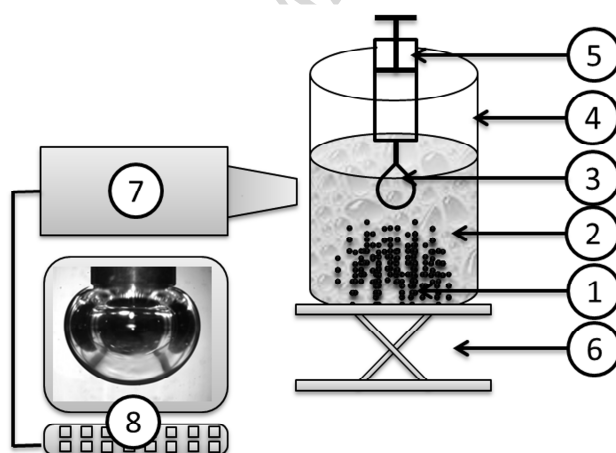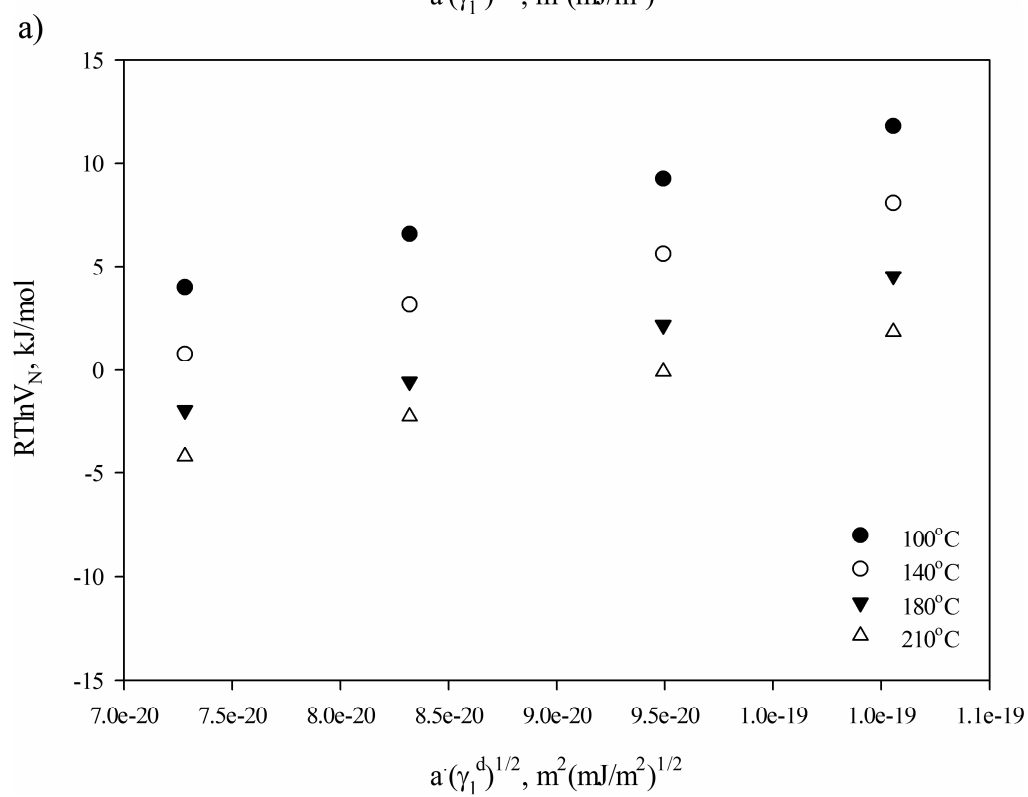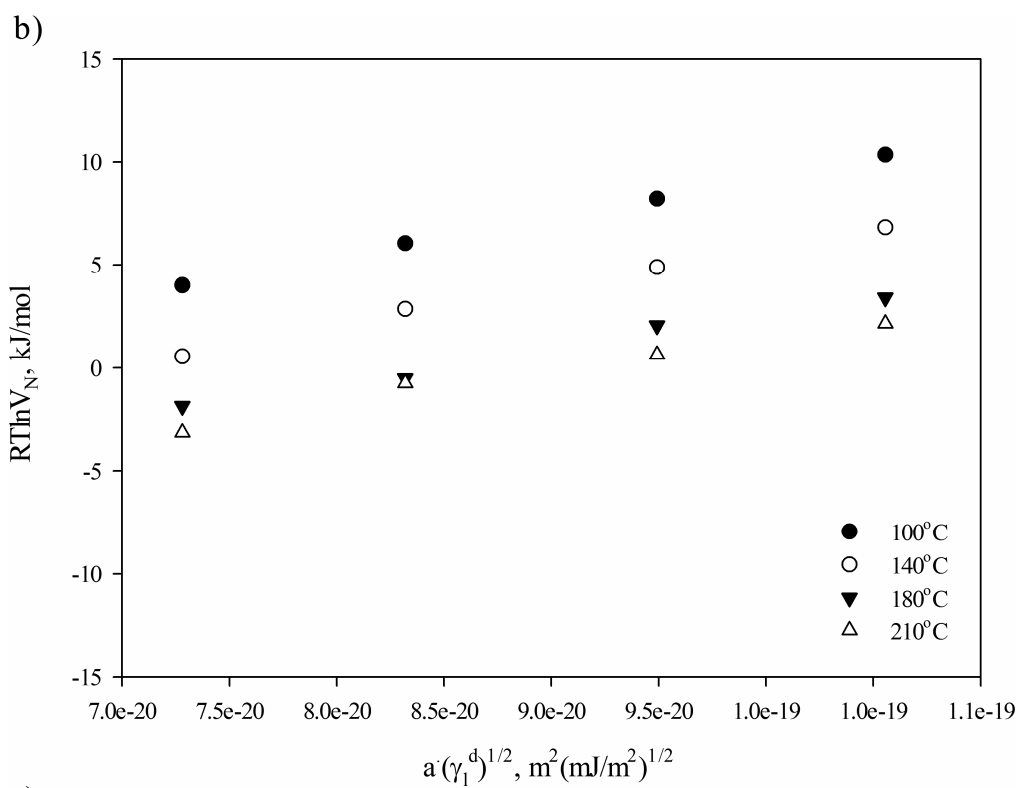

Figure 2 Experimental rig for investigations of the attachment of particles to the single

bubble: 1 – particles, 2 – liquid , 3 - bubble, 4 - glass container, 5 – syringe, 6 – adjustable

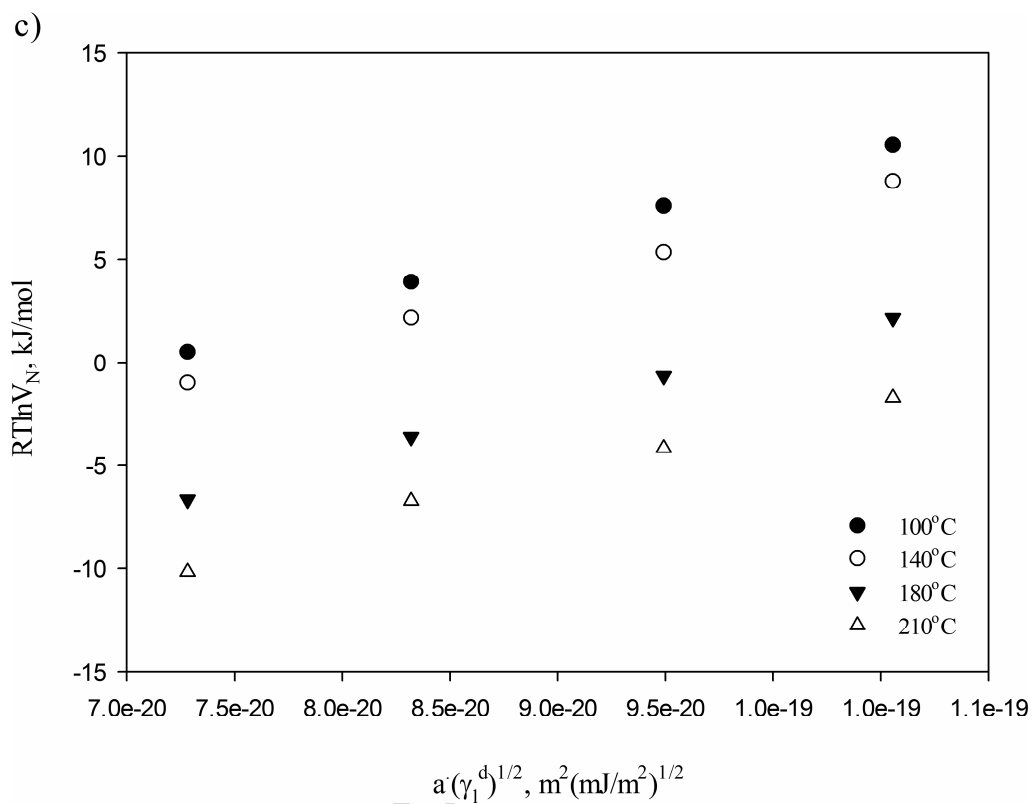height stand, 7-8 – video microscope computer system

b)

a)

c)

Figure 3 The adsorption free energies of the alkanes on the a) Al_2O_3, b) SiO_2 and c) ZrO_2 as a
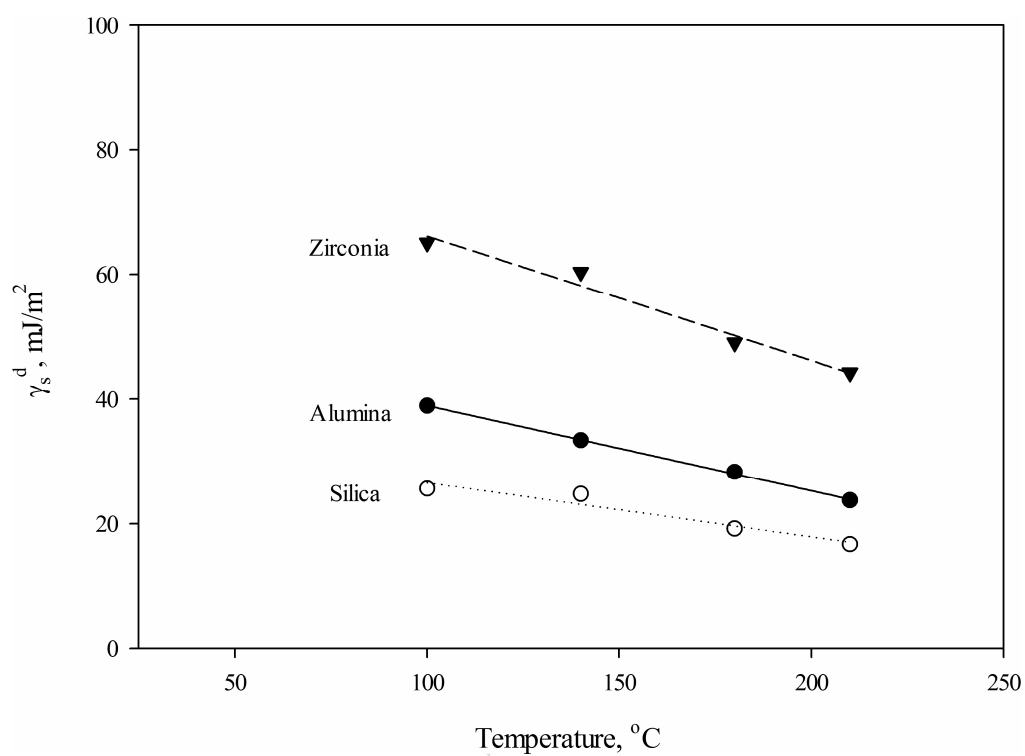
function of temperature

Figure 4 Dispersive components of particles surface energy as a function of temperature
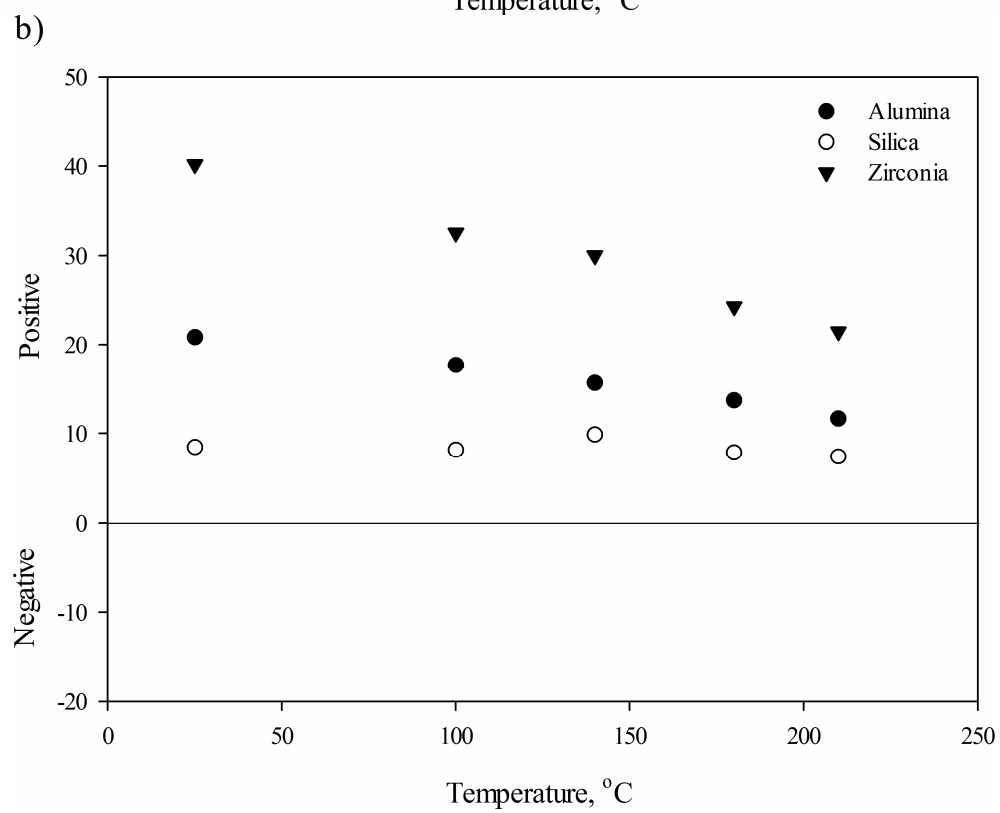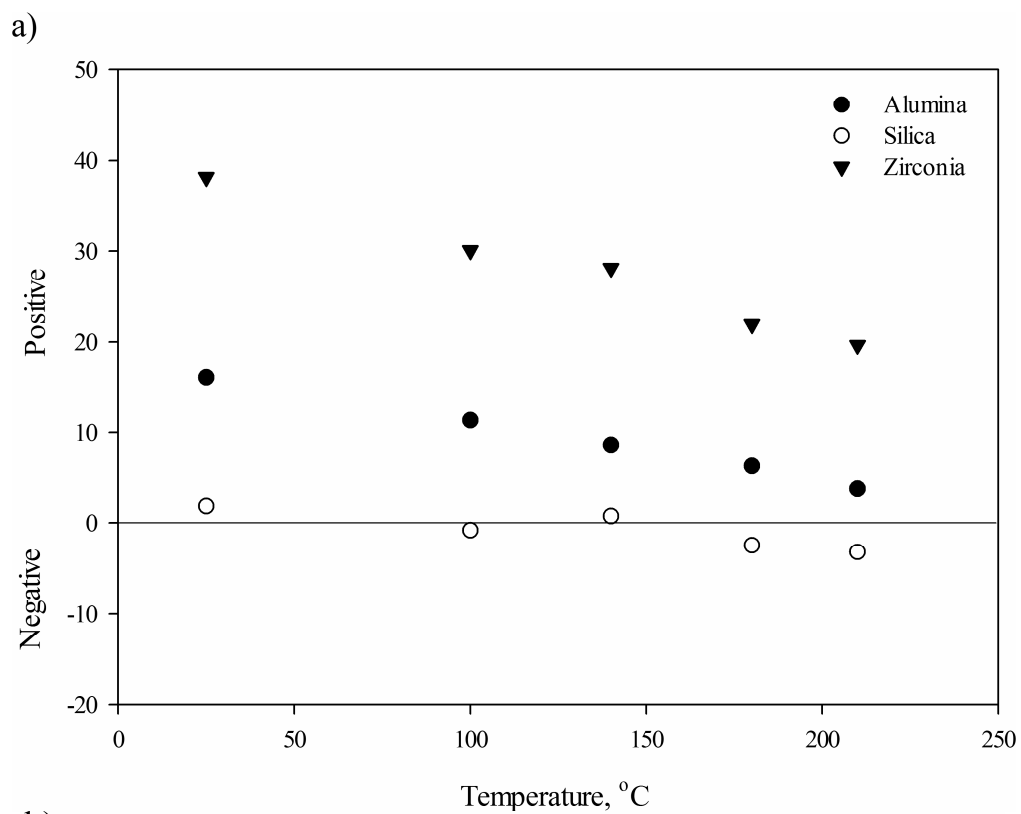
a)

b)

Figure 5 Change of energy (ΔE) in the three phase system upon particles detachment from the

bubble in a) paraffin oil and b) decane

a) Al$_2$O$_3$ SiO$_2$ ZrO$_2$

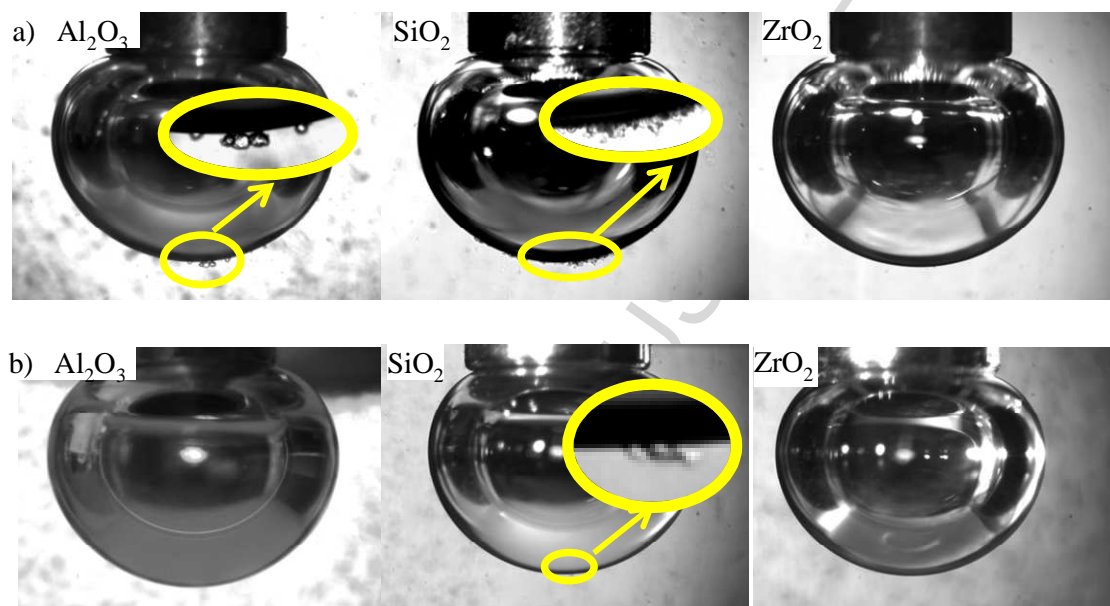b) Al$_2$O$_3$ SiO$_2$ ZrO$_2$

Figure 6 Particles and bubble in a) paraffin oil and b) decane (the size of each image
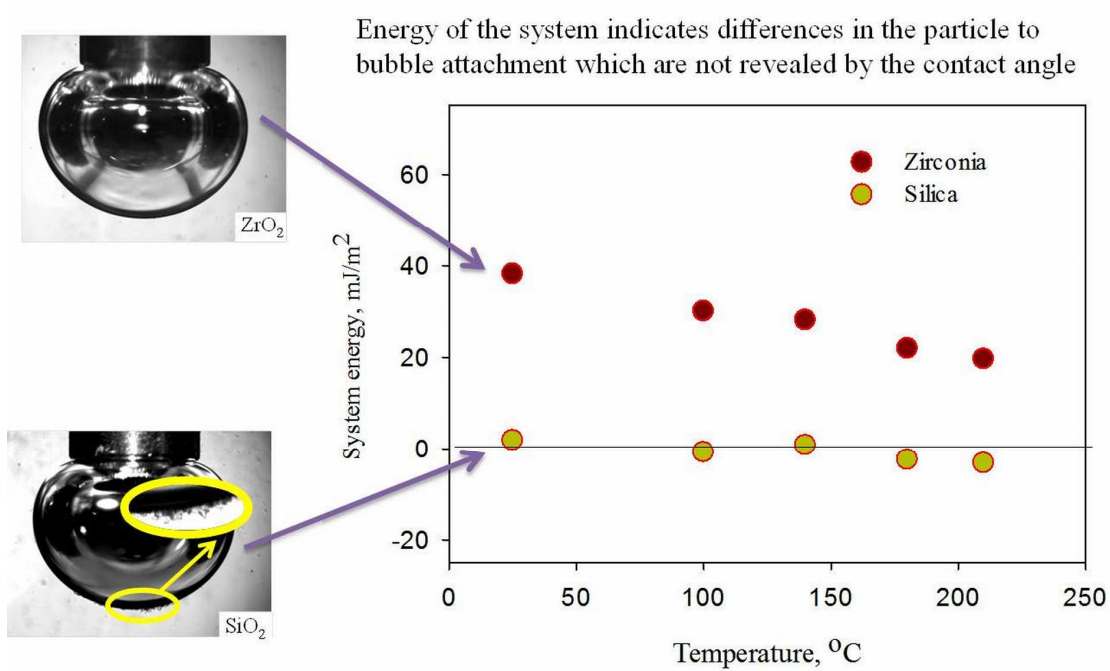
3.6x2.8mm)

Table 1. Properties of liquids used in the experiments (Rodriguez *et al.* 1997; Liu *et al.* 1998; Yaws 2003)

Liquid probes	a, Å	Surface tension $(=\gamma_l^d)$, mN/m	Density, kg/m^3	Viscosity, mPa·s
n-hexane	51.1	18.4	656	0.296
n-heptane	57	20.3	682	0.390
n-octane	63	21.3	699	0.511
n-nonane	69	22.7	715	0.672
n-decane	-	23.8	728	0.863
paraffin oil	-	31	873	103

Table 2. Temperature, pressure and flow rates of inert gas carrying solvent probe

		Al_2O_3	SiO_2	ZrO_2
Mass, g		0.4593	0.3691	0.5926
P, kPa		511	344	172
Flow rates ml/min	100°C	10	4	33
	140°C	8.82	3.66	29.9
	180°C	7.69	3.22	25
	210°C	7.14	3	18.7

Energy of the system indicates differences in the particle to bubble attachment which are not revealed by the contact angle

Graphical abstract

Research Highlights:

- Thermodynamical description of the interfacial/surface energies at the three phase contact
- Position of particles in a three phase solid/gas/liquid systems in a function of surface/interfacial energies
- Particles to bubbles attachment in organic liquids