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Sustainable Chemistry

Efficient and Sustainable Production of Alumina by Electrolysis of Sodium Carbonate**

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Aluminium is a leading material for the expanding global economy and its precursor alumina has been produced by extraction of bauxite ores using Bayer and sinter processes for over 100 years. The Bayer process involves digesting and leaching the ores using a hot alkali solution and precipitating aluminum hydroxide from the supersaturated aluminate leachate (green liquor) using aluminum hydroxide seed particles.[1] The caustic liquor remaining after precipitation (spent green liquor) is concentrated by evaporation and recycled back to the extraction step (Figure 1 A). The sinter process consists of sintering the ores with sodium carbonate and calcium oxide at above 1000 °C, leaching the sinter mass with water (or dilute NaOH solution) and precipitating $Al(OH)_3$ with carbon dioxide, concentrating the spent green liquor by evaporation, and circulating the concentrate to the next sinter step (Figure 1 B). The sinter process is more effective for poor-grade diaspore ores than the Bayer process, but its high energy consumption makes it uneconomical compared to the Bayer process and its environmental impact has been a critical issue. The Bayer process is relatively simple because of the ease of automation and delivers 90 % of the world-wide production of alumina. However, the seed precipitation of the Bayer process is typically very slow (generally it takes 48–70 h) and requires a large quantity of aluminum hydroxide seeds (seed ratios of 1–2) while only up to 50 % of sodium aluminate in the green liquor is decomposed into aluminum hydroxide precipitates.[2] Consequently, large tonnages of sodium aluminate remain in the circuit of the process. The presence of a large amount of aluminate in the Bayer liquor has significant adverse effects on the leaching efficiency of ore digestion. These problems are the major factors for the loss of productivity of the Bayer-based plants.[1b,2b,d,3] In addition, the Bayer process becomes uneconomical for processing diaspore ores of alumina-to-silica (A/S) mass ratios < 9.[4]

Since the 1970s, the world-wide production of minerals and metals from degrading natural resources has increased. The global production of alumina increased at an average rate of 3.3 % per year while the Chinese production of alumina grew at an average rate of 25 % between 2001 and 2007. The aluminum industry is one of the major high-pollution and energy-intensive industries. With increasing environmental constraints, continuously increasing demand for aluminum and at the same time the depletion of high-grade bauxite ores, the development of efficient and sustainable production processes for alumina is of great significance.[1b] The key to improving the efficiency of the Bayer process is to increase the efficiency of aluminate decomposition and the precipitation rate of aluminum hydroxide.[1b,6] The strategies include addition of surfactants, glucose or methanol, to the green liquor.[2b,d] However, the improvement is limited because of the inherent equilibrium between $Al(OH)_4^-$, $Al(OH)_3$, and OH^- of the seeded precipitation [Eq. (1)],[3]

$$NaAl(OH)_4 + \beta Al(OH)_3(seed) \rightleftharpoons (\beta+1)Al(OH)_3\downarrow + NaOH \qquad (1)$$

where β is the $Al(OH)_3$ seed ratio. In contrast, the precipitation rate of CO_2 carbonation in the sinter process is fast and the decomposition efficiency of aluminate is greater than 95 % [Eq. (2)].[7]

$$2\,NaAl(OH)_4 + CO_2 \rightarrow Al(OH)_3\downarrow + Na_2CO_3 + 4\,H_2O \qquad (2)$$

When CO_2 carbonation and precipitation is applied in the Bayer process, the causticization of Na_2CO_3 to NaOH is required to continue the cycle of operation. As early as in 1885, the causticization of Na_2CO_3 with lime [Eq. (3)] has been proposed.

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2\,NaOH + CaCO_3\downarrow \qquad (3)$$

However, the lime causticization requires a large quantity of quicklime (CaO) or slaked lime ($Ca(OH)_2$) and the lime efficiency is relatively low resulting in a fairly diluted NaOH solution.[8] In addition, the particles of the $CaCO_3$ precipitate are very fine. Therefore, separation and treatment of large tonnages of $CaCO_3$ precipitate are difficult.[9] Furthermore, the CO_2 carbonation has shortcomings because of a mass transfer limitation at the gas–liquid interface and local over-

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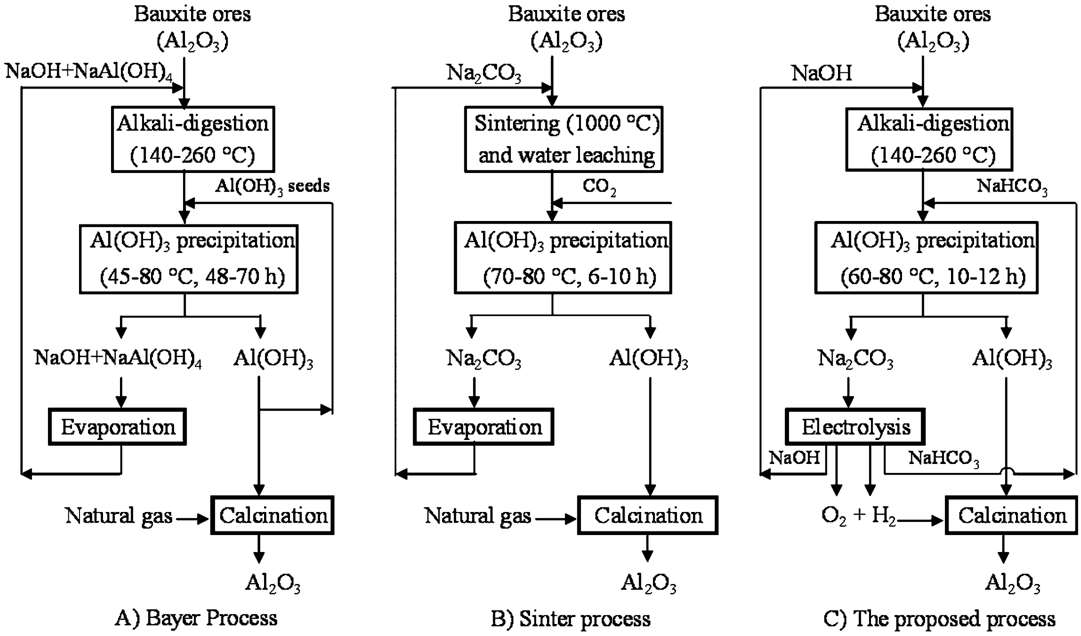

Figure 1. simplified flow chartS of A) the Bayer, B) sinter, and C) proposed processes.

carbonation at the gas–liquid interface, leading to co-precipitation of dawsonite ($Na_2O{\cdot}Al_2O_3{\cdot}2\,CO_2{\cdot}n\,H_2O$) and difficulties in controlling the formation of dawsonite during the precipitation process.[10] Consequently, the CO_2 carbonation–precipitation process has not been implemented in the Bayer plants despite its high decomposition efficiency and fast precipitation rate. To avoid the mass transfer limitation of CO_2 carbonation at the gas–liquid interface, we proposed $NaHCO_3$ carbonation for precipitating aluminum hydroxide from the caustic liquor [Eq. (4)].[11]

$$NaAl(OH)_4 + NaHCO_3 \rightarrow Al(OH)_3\downarrow + Na_2CO_3 + H_2O \qquad (4)$$

Recently, the validity of $NaHCO_3$ carbonation was also tested for precipitating $Al(OH)_3$ from synthetic caustic liquor of the sinter process.[12] The $NaHCO_3$ carbonation and precipitation in the Bayer process requires the causticization of the Na_2CO_3 liquor to regenerate NaOH and $NaHCO_3$. Clearly, the lime causticization does not meet this particular requirement. Here we propose that the electrolysis of the Na_2CO_3 solution is incorporated into the Bayer process for production of alumina from bauxite ores (Figure 1 C). During electrolysis of the Na_2CO_3 solution a concentrated NaOH solution is regenerated but also $NaHCO_3$, H_2, and O_2 are produced. The pure and concentrated NaOH solution produced by electrolysis is used for the digestion of bauxite ores. Thus the problems associated with the Bayer liquor ($NaOH/NaAl(OH)_4$ ratio of 2:1) in the digestion are eliminated. Unlike the slow process of aluminum hydroxide seeded precipitation in the Bayer process, the kinetics of $NaHCO_3$ carbonation and precipitation is fast and readily controlled. Hydrogen gas obtained by electrolysis can be used as fuel for the calcination of aluminum hydroxide, which is a clean and green process with no generation of greenhouse gas (GHG). Oxygen can be used for oxygen-enriched air combustion, which saves energy by 26.1 % when the O_2 concentration in the air is increased from 21 % to 30 %.[13] The simplified flow chart of the proposed process is compared with the Bayer and sinter processes in Figure 1, and the three processes are compared in Table S1 in the Supporting Information.

The electrolytic cell is illustrated in Figure S1 in the Supporting Information, which is similar to that used in the chlor alkali industry. Different anode materials (RuO_2/Ti, IrO_2/Ti, IrO_2-Co_2O_3/Ti and RuO_2-Ni_2O_3/Ti) and the influence of the temperature of the electrolyte have been investigated. The IrO_2-Co_2O_3/Ti anode-RuO_2/Ni cathode pair showed a relatively low cell voltage and good stability (see Figure S2A in the Supporting Information). The cell voltage decreases sharply with increasing temperature of the electrolyte solution and does not change significantly above 70 °C (see Figure S2B in the Supporting Information). This temperature is well-fitted to the precipitation step where the temperature is generally between 60 and 80 °C. Concentrations of 6.5 M NaOH and 1.3 M $NaHCO_3$ were obtained at flow rates of $1\,L\,h^{-1}$ for water and $8.5\,L\,h^{-1}$ for a 1.5 M Na_2CO_3 solution under the optimum operating conditions (see Figure S3 in the Supporting Information) and a steady supply of 6.5 M NaOH and 1.3 M $NaHCO_3$ at a current density of $1000\,A\,m^{-2}$ and cell voltage of 2.55 V was achieved with a current efficiency of $96 \pm 2\,\%$ (see Figure S4 in the Supporting Information).

The leaching efficiency and capacity are used for evaluation of the digestion/leaching performance, and the circulation efficiency (E) describes the amount of alumina produced per ton caustic soda (Na_2O) in one cycle of the process. The concentration of caustic soda (Na_2O), the mole ratio (MR) of Na_2O to Al_2O_3 in the caustic liquor before $(MR)_m$ and after ore digestion $(MR)_a$ in the Bayer process determine the digestion efficiency, leaching capacity, the stability of supersaturated green liquor, and circulation efficiency. In general, $(MR)_m$ has to be greater than 2.6 to maximize the digestion efficiency, whereas $(MR)_a$ has to be between 1.2 and 1.6 to find a compromise with respect to the stability of the green liquor and the concentration of aluminate. The decomposing efficiency of aluminate in the Bayer process is $< 50\%$.[10,14] Thus, $(MR)_m$ is $< 2(MR)_a$. The circulation efficiency (E) equals $1.645[(MR)_m-(MR)_a]/[(MR)_m(MR)_a]$ and therefore, the E value of the Bayer process is $< 0.82/(MR)_a$. In contrast, the decomposition efficiency of aluminate in the green liquor by $NaHCO_3$ is greater than 98% and the remaining Al concentration after precipitation can be as low as 0.5 mgL^{-1}. Thus $(MR)_m \gg (MR)_a$ and the E value equals approximately $1.645/(MR)_a$ in the proposed process. As a result, the E value is at least twice that of the Bayer process. The leaching efficiency increases with increasing NaOH concentration (see Figure S5 in the Supporting Information) and the leaching capacity and circulation efficiency of the proposed process are doubled relative to the Bayer process (Table 1). The quality of aluminum hydroxide is critical for the production of high-quality alumina and the quality parameters include loss on ignition (LOI), content of impurities (Na_2O, SiO_2, Fe_2O_3), particle morphology, size distribution, and the fraction of fine particles (< 45 µm).[7,10] Two types of $Al(OH)_3$ crystals (floury and sandy) are formed in the precipitation. Sandy and coarse alumina crystals are more desirable in modern aluminum industry partially because floury and fine $Al(OH)_3$ particles can cause severe dusting and handling difficulties during the calcination process.[6,14b,15] In the Bayer process, the precipitation lasts for 48–70 h and the decomposition efficiency of aluminate is controlled at around 40% to obtain coarse and sandy gibbsite particles.[2a,d] The decomposing efficiency of aluminate increases with increased loading of the $NaHCO_3$ solution and is greater than 98% when the stoichiometric dose of $NaHCO_3$ is added (see Figure S6A in the Supporting Information). The remaining concentration of Al in the Na_2CO_3 solution after the precipitation is 210 mgL^{-1} at the stoichiometric dose of $NaHCO_3$ and decreases to 0.5 mgL^{-1} when the $NaHCO_3$ solution is over-dosed by 11% (see Figure S6B in the Supporting Information). The concentration of impurities can be reduced to µgL^{-1} level by further purification treatments. The precipitation rate is one of the important factors for the growth, agglomeration, and nucleation of aluminum hydroxide crystals.[7,12] The rate of $NaHCO_3$ carbonation and precipitation can be readily controlled by adjusting the total reaction time through the loading rate of the $NaHCO_3$ solution. The total reaction time does not affect the LOI and the concentration of SiO_2 and Fe_2O_3 whereas the concentration of Na_2O and the fraction of fine particles decrease with increasing total reaction time (see Figure S7 in the Supporting information). A total reaction time of 10–12 h was found to be optimum and thus the loading rate of 1.2 M $NaHCO_3$ for the treatment of one liter of a typical green liquor (mixtures of 4.5 M $NaAl(OH)_4$ and 2 M NaOH) was calculated to be 0.54 Lh^{-1}. Under these conditions, more than 97% of the sandy $Al(OH)_3$ crystals (Figure 2A) were obtained with particle sizes of 80–320 µm (Figure 2B).

Table 1: Comparison of the Bayer and proposed processes for the digestion of different types of bauxite ores (the volume of the leaching solution was 1 L).

	Bayer process[a]		Proposed process[b]	
Type of ore	A/S 6.2	A/S 8.6	A/S 6.2	A/S 8.6
ore digested [g]	255	243	498	454
NaOH concentration after digestion [M]	1.6	1.62	1.56	1.53
$NaAl(OH)_4$ concentration [M]	4.63	4.69	4.72	4.77
leaching efficiency [%]	75	76.5	79	81.8
leaching capacity of Al_2O_3 [gL^{-1}]	118	123	243	246
ratio of Na_2O to Al_2O_3 $(MR)_a$	1.35	1.34	1.33	1.32
E [in tons of Al_2O_3/tons of Na_2O]	0.53	0.54	1.24	1.24

[a] The typical composition of the spend green liquor of the Bayer process is 4 M NaOH + 2.5 M $NaAl(OH)_4$. [b] The caustic liquor for digestion is 6.5 M NaOH.

The proposed process was shown in a small pilot unit at a capacity of 10 kg alumina per day using diaspore ore (A/S 7.7) as feed. The percentage of the impurities in the sandy alumina product was SiO_2 0.018%, Fe_2O_3 0.012%, Na_2O 0.223%, and LOI 0.1% (this purity exceeds the grade one alumina standard which is 0.02, 0.02, 0.5, and 1%, respectively). The fraction of fine particles (< 45 µm) is 8.2% and the attrition index is 9.1 (the fraction of < 45 µm particles and the attrition index for sandy grade alumina are required to be less than 10% and 10, respectively). The energy consumption was

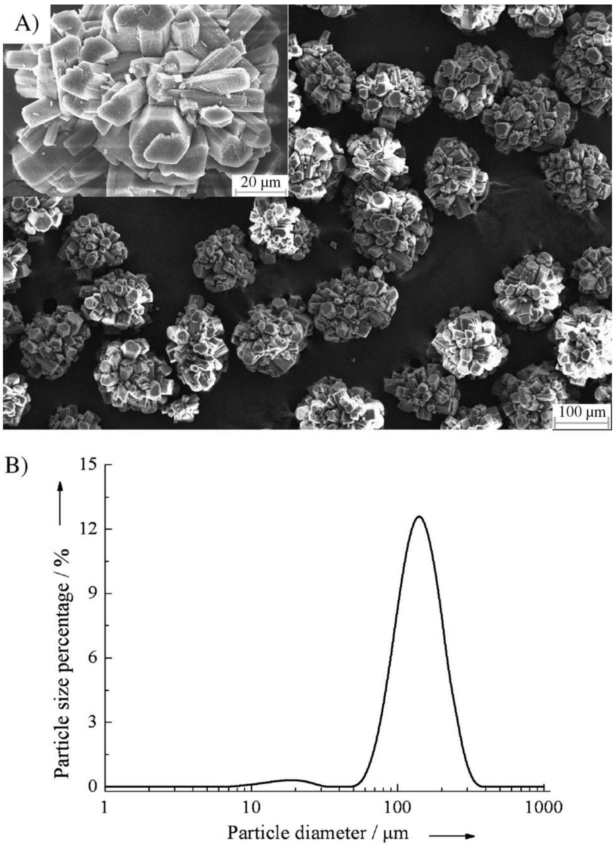

Figure 2. A) A scanning electron microscopic image and B) the particle size distribution of the $Al(OH)_3$ product.

analyzed on the basis of the principle of materials flow, the consumption factor data reported in the literature, and the production data from Henan Branch of Aluminum Corporation of China.[16] The efficiency, energy consumption, and CO_2 emission of the Bayer, sinter, and the proposed processes are compared in Table 2 and the energy input at each step of the Bayer and proposed processes is given in Table S2 in the Supporting Information. For production of aluminum hydroxide, the energy consumption of the proposed process is 10.5% higher than for the Bayer process and 66.3% lower than for the sinter process (9.58, 8.67, and 28.41 GJ for the proposed, the Bayer, and sinter processes, respectively, see Table 2 and Table S2 in the Supporting Information). The major contributions to the consumption of energy for alumina production by the Bayer process come from digestion, precipitation, evaporation, and calcination, and the total energy consumption is 12.05 GJ per tone alumina (see Table S2 in the Supporting Information). The total energy consumption of the Bayer process mainly depends on the type of bauxite ores and covers a range of 9.3–14.7 GJ per tone alumina world-wide in 2009.[17] The electrolysis requires the major part of the energy input in the proposed process and an electric energy consumption of 6.66 GJ corresponds to 69.5% of the total energy consumption. When the energy for calcination is accounted, the proposed process saves 18.5% energy input relative to the Bayer process. Despite a substantial saving of energy, an independent evaluation of the cost-effectiveness analysis indicated that the costs for alumina production by the proposed process were estimated to be about 15% higher than the costs of the Bayer process. The higher costs are mainly due to high electricity charges. Nevertheless, the proposed process is competitive when sufficient and low-cost renewable electricity is available and particularly when additional factors, such as human health issues and environmental costs, are considered.[18]

Table 2: Comparison of the Bayer, sinter, and proposed processes (data are for the production of one tone of calcined alumina).

Item	Bayer process	Sinter process	Proposed process
bauxite ore required [t]	1.9–2.3	1.7–2.1	1.8–2.2
digestion temperature [°C]	140–260	>1000	140–260
leaching efficiency [%]	≈ 75	≈ 95	≈ 80
aluminate decomposition [%]	40–50	>95	>95
precipitation time [h]	48–70	6–8	10–12
E (ton Al_2O_3/ton Na_2O)	0.59	1.22	1.24
H_2 produced [kg]	NA	NA	25.4
O_2 produced [kg]	NA	NA	203
total energy consumption [GJ][a]	12.05	31.79	9.81
for aluminum hydroxide	8.67	28.41	9.58
for $Al(OH)_3$ calcination	3.38[b]	3.38	0.23[c]
CO_2 emission [t][d]			
coal electricity system	1.29	3.11	1.982
clean-energy electricity	1.07	2.83	0.22

[a] For the major steps of the processes and the details of the Bayer and proposed processes are given in Table S2 in the Supporting Information. [b] Using natural gas as fuel. [c] The produced hydrogen (25.4 kg) is equivalent to 3.15 GJ in accordance with a heating value of 124 MJ kg^{-1} H_2 at 800 °C. The energy input for the calcination is 3.38 GJ. Therefore, an external energy of 0.23 GJ is needed to supplement the hydrogen calcination. [d] Including the emissions from calcination of aluminum hydroxide, coal combustion for electricity, heating, and steam for evaporation. The calculation of CO_2 emissions was based on 2.7 tons CO_2 per ton coal on combustion and 0.88 tons CO_2 per 1000 kWh by coal electricity.[19]

When the electricity of alumina plants is supplied by coal power, the respective CO_2 emission is 1.29, 3.11, and 1.982 tons by the Bayer, sinter, and proposed processes for the production of 1 tone of calcined alumina. When the electricity is supplied by renewable and clean energies (such as solar, wind, hydro or geothermal energies), the CO_2 emission will be reduced by 88.8% (1.982 to 0.22 tons) in the proposed process, 17.0% (1.29 to 1.07 tons) in the Bayer process, and 9.0% (3.11 to 2.83 tons) in the sinter process. In contrast, the CO_2 emission is reduced by 79.3 and 92.2% when the proposed process is compared to the Bayer and sinter processes, respectively. Energy generation through renewable and clean approaches is increasing at an annual rate of 7.2% relative to 1.6% for nonrenewable energies.[20] In China, the electricity from renewable and nuclear energies increased by 49.1% from 2006 to 2009 and this represented 25–27% of the total electricity supplies in 2009.[21] The clean-energy electricity represented 29% of the total electricity in the United States and the world average was 31% (data of 2008).[21b,22] The renewable and clean energy is anticipated to replace fossil fuels[23] and a recent study[24] shows that renewable energies could meet all global energy demands by more than one order of magnitude by 2050 at costs similar to current carbon-based fuels. The World Wild Found for Nature (WWF) just issued the energy report 2011 stating that all energy obtained from renewable sources could become cost-effective by 2050.[25] In this context, the proposed process for production of alumina is more environmentally and economically viable and sustainable than the current practice of alumina production.

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[1] a) B. Dash, B. C. Tripathy, I. N. Bhattacharya, S. C. Das, C. R. Mishra, B. K. Mishra, *Hydrometallurgy* **2009**, *95*, 297–301; b) Alumina Technology Roadmap, International Aluminum Institute, May **2006**. http://www.world-aluminium.org/cache/fl0000224.pdf.

[2] a) S. Veesler, R. Boistelle, *J. Cryst. Growth* **1993**, *130*, 411–415; b) H. Watling, J. Loh, H. Gatter, *Hydrometallurgy* **2000**, *55*, 275–288; c) H. Li, J. Addai-Mensah, J. C. Thomas, A. R. Gerson, *J. Cryst. Growth* **2005**, *279*, 508–520; d) Y. Zhang, S. Zheng, H. Du, H. Xu, S. Wang, Y. Zhang, *Hydrometallurgy* **2009**, *98*, 38–44.

[3] a) Y. Zhang, Y. Li, Y. Zhang, *J. Chem. Eng. Data* **2003**, *48*, 617–620; b) G. S. Gontijo, A. C. B. d. Araújo, S. Prasad, L. G. S. Vasconcelos, J. J. N. Alves, R. P. Brito, *Miner. Eng.* **2009**, *22*, 1130–1136.

[4] R. C. Kirby, A. S. Prokopovitsh, *Science* **1976**, *191*, 713–719.

[5] J. B. Rosenbaum, *Science* **1976**, *191*, 720–723.

[6] A. R. Gerson, *Prog. Cryst. Growth Charact. Mater.* **2001**, *43*, 187 – 220.
[7] Z. Wang, S. Bi, Y. Yang, Z. Yuan, *J. Cryst. Growth* **2005**, *274*, 218 – 225.
[8] a) K. A. Kobe, J. A. Wilkinson, *J. Ind. Eng. Chem.* **1953**, *45*, 307 – 312; b) S. C. Libby, US patent 4,451,443, **1984**.
[9] M. Wellington, F. Valcin, *Ind. Eng. Chem. Res.* **2007**, *46*, 5094 – 5099.
[10] Q. Zhou, D. Peng, Z. Peng, G. Liu, X. Li, *Hydrometallurgy* **2009**, *99*, 163 – 169.
[11] Y. Niu, P. Wan, Z. Lu, J. Pan, Y. Chen, Y. Sun, G. Meng, H. Zhang, R. Jin, F. Zhao, China Patent CN101249976, **2008**.
[12] Y. Li, Y. Zhang, C. Yang, Y. Zhang, *Hydrometallurgy* **2009**, *98*, 52 – 57.
[13] K. K. Wu, Y. C. Chang, C. H. Chen, Y. D. Chen, *Fuel* **2010**, *89*, 2455 – 2462.
[14] a) B. Gnyra, N. Brown, *Powder Technol.* **1975**, *11*, 101 – 105; b) D. Ilievski, I. Livk, *Chem. Eng. Sci.* **2006**, *61*, 2010 – 2022.
[15] H. Li, J. Addai-Mensah, J. C. Thomas, A. R. Gerson, *Colloids Surf. A* **2003**, *223*, 83 – 94.
[16] a) B. Hyman, T. Reed, *Energy* **1995**, *20*, 593 – 606; b) J. P. Andersen, B. Hyman, *Energy* **2001**, *26*, 137 – 159; c) L. Liu, L. Aye, Z. Lu, P. Zhang, *Energy* **2006**, *31*, 1870 – 1882; d) Q. B. Yu, Z. W. Lu, J. J. Cai, *J. Iron Steel Res. Int.* **2007**, *14*, 46 – 51.
[17] International Aluminum Institute, https://stats.world-aluminium.org/iai/stats_new/formServer.asp?form = 8, September **2010**.
[18] M. Z. Jacobson, W. G. Colella, D. M. Golden, *Science* **2005**, *308*, 1901 – 1905.
[19] a) Y. H. Zheng, Z. F. Li, S. F. Feng, M. Lucas, G. L. Wu, Y. Li, C. H. Li, G. M. Jiang, *Renewable Sustainable Energy Rev.* **2010**, *14*, 3132 – 3139; b) *International energy agency* http://www.uneptie.org/ozonaction/information/mmcfiles/6077-e-IEA_Energy_Efficiency_Air_Conditioners.pdf, November **2007**.
[20] J. M. Tour, C. Kittrell, V. L. Colvin, *Nat. Mater.* **2010**, *9*, 871 – 874.
[21] a) E. Martinot, *Front. Energy Power Eng. China* **2010**, *4*, 287 – 294; b) http://www.ren21.net/globalstatusreport/REN21_GSR_2010_full.pdf.
[22] U. S. Energy Information Administration. http://www.eia.gov/FTPROOT/electricity/034808.pdf, August **2010**.
[23] N. Armaroli, V. Balzani, *Angew. Chem.* **2007**, *119*, 52 – 67; *Angew. Chem. Int. Ed.* **2007**, *46*, 52 – 66.
[24] a) M. Z. Jacobson, M. A. Delucchi, *Energy Policy* **2011**, *39*, 1154 – 1169; b) M. A. Delucchi, M. Z. Jacobson, *Energy Policy* **2011**, *39*, 1170 – 1190.
[25] World Wide Fund For Nature. http://assets.panda.org/downloads/101223_energy_report_final_print_2.pdf, **2011**.