

## CARBOTHERMIC REDUCTION OF ALUMINA BY NATURAL GAS TO ALUMINUM AND SYNGAS: A THERMODYNAMIC STUDY

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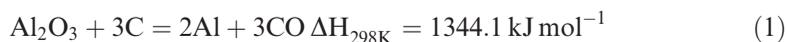
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*The carbothermic reduction of alumina to aluminum by methane is analyzed by thermochemical equilibrium calculations in order to determine its thermodynamic constraints. Calculations predict that in the temperature range 2300–2500° C at 1 bar pressure, the reaction  $Al_2O_3 + 3CH_4 = 2Al + 6H_2 + 3CO$  should occur without significant interference by the formation of unwanted byproducts such as  $Al_2O$ ,  $Al_4C_3$ , and Al-oxycarbides, and with higher yields than by using solid carbonaceous compounds as reducing agent. The reaction was examined for several initial  $Al_2O_3/CH_4$  molar ratios. The proposed process may be carried out in a fluidized bed reactor using concentrated solar energy, induction furnaces, or electric discharges as sources of high-temperature process heat. An important advantage of such a process would be the coproduction of syngas, with the molar ratio  $H_2/CO = 2$ , suitable for the synthesis of liquid hydrocarbon fuels and polymeric materials.*

**Keywords:** Al-oxycarbides, alumina, aluminum, carbothermic, exergy, methane, natural gas, syngas

### INTRODUCTION

Much effort has been spent to achieve the carbothermic reduction of alumina to aluminum as an alternative to the electrolytic Hall–Héroult process (Choate and Green 2006). In most of these studies, the carbonaceous reducing agent has been a solid, such as activated charcoal (Murray, Steinfeld, and Fletcher 1995; Halmann, Frei, and Steinfeld 2007; Kruesi et al. 2011). These were thus, at least formally, solid–solid reactions, although their mechanism may include gas–solid reaction steps (Cox and Pidgeon 1963; Fruehan, Li, and Cargin 2004). Using a solid carbon source or  $CH_4$  as reducing agents, the overall reactions are



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Only a few studies have considered reaction (2). The reduction of  $\text{Al}_2\text{O}_3$  to Al under Ar and  $\text{CH}_4$  at atmospheric pressure was studied experimentally in a radio-frequency generated induction-coupled plasma at above  $10,000^\circ\text{C}$ . The reduction products collected on water-cooled probes contained Al and  $\text{Al}_4\text{C}_3$  (Rains and Kadlec 1970). Attempts were made to achieve the reduction by  $\text{CH}_4$  of  $\text{Al}_2\text{O}_3$  contained in a graphite crucible under concentrated solar irradiation. However, at  $1400^\circ\text{C}$ , only cracking of  $\text{CH}_4$  to  $\text{H}_2$  and carbon was observed (Petrasch 2002). Thermochemical calculations on the equilibrium composition reached from an initial reaction mixture of  $\text{Al}_2\text{O}_3 + 4\text{CH}_4 + 0.4\text{O}_2$  at 1 bar predicted 91% conversion to Al at  $2400^\circ\text{C}$  (Halmann, Frei, and Steinfeld 2007). Equilibrium compositions as a function of temperature and enthalpies of reaction described in the present work were calculated using the HSC code (HSC Chemistry Computer Code). Similar results were obtained using the FactSage code (FactSage), except for the temperature region of  $1500\text{--}2300^\circ\text{C}$ , at which the HSC code listed  $\text{Al}_2\text{CO}$ ,  $\text{Al}_4\text{CO}_4$ , carbon, and  $\text{Al}_2\text{O}(\text{g})$ , while the FactSage code instead listed  $\text{Al}_4\text{C}_3(\text{s})$ ,  $\text{C}(\text{gr})$ , and  $\text{Al}_2\text{O}(\text{g})$ . In the region important for  $\text{Al}(\text{g})$  production,  $2300\text{--}2500^\circ\text{C}$ , both codes predicted  $\text{H}_2(\text{g})$ ,  $\text{CO}(\text{g})$ , and  $\text{Al}(\text{g})$  as practically the only products. The reaction onset temperature was taken at about 0.001% conversion of the  $\text{Al}_2\text{O}_3$  to the metal.

## THERMODYNAMIC ANALYSIS

### The System $\text{Al}_2\text{O}_3 + 3\text{CH}_4$

The temperature dependence of the equilibrium composition for the initial reaction mixture of  $\text{Al}_2\text{O}_3 + 3\text{CH}_4$  is presented in Figure 1. At  $2500^\circ\text{C}$ , the equilibrium

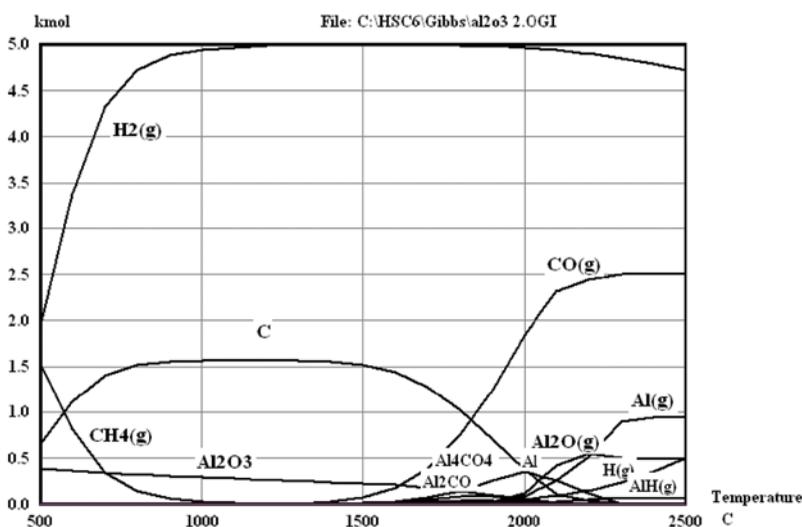
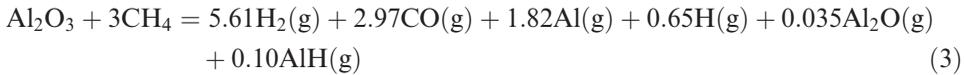
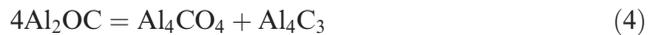


Figure 1 System  $\text{Al}_2\text{O}_3 + 3\text{CH}_4$  at 1 bar (color figure available online).

composition is represented by the reaction



The enthalpy of the reaction at 2500°C is 1978.9 kJ/mol  $\text{Al}_2\text{O}_3$ . In the temperature range 1500–1800 K, the predominant carbon species is C(gr), probably due to dissociation (cracking) of methane. From 1700 to 2300°C, the formation of aluminum oxycarbides  $\text{Al}_2\text{OC}$  and  $\text{Al}_4\text{CO}_4$  and of  $\text{Al}_2\text{O}(\text{g})$  is thermodynamically favored. In experiments on the  $\text{Al}_2\text{O}_3 + 3\text{C}$  reaction at 1 bar under induction furnace heating, the solid products isolated on the cool reactor wall contained Al,  $\text{Al}_2\text{OC}$ ,  $\text{Al}_4\text{CO}_4$ , and  $\text{Al}_4\text{C}_3$  as identified by XRD analysis (Halmann, Frei, and Steinfeld 2007).  $\text{Al}_2\text{OC}$  had been reported to decompose at below 1715°C, according to the reaction (Lihmann, Zambetakis, and Daire 1989)



producing aluminum carbide. The formation of  $\text{Al}_4\text{CO}_4$  can also be explained by the reaction of  $\text{Al}_2\text{OC}$  with alumina (Lihmann, Zambetakis, and Daire 1989)



Pertinent to aluminum production is the lowest temperature at which the production of gaseous Al will be accompanied only by the syngas mixture of  $\text{H}_2$  and CO (and a minor amount of  $\text{Al}_2\text{O}$ ), 2300°C. In the temperature range 2200–2500°C, the  $\text{H}_2/\text{CO}$  molar ratio of the syngas mixture would be 2.1–1.9, suitable for methanol synthesis or for Fischer–Tropsch conversion to liquid hydrocarbons. The onset of Al(g) production (calculated by the FactSage code) occurs at a considerably lower temperature for the reduction of alumina by methane (Eq. 2) than by solid carbon (Eq. 1), as shown in Table 1. This onset of Al vapor pressure obviously occurs at a much lower temperature than the boiling point of aluminum metal, 2519°C.

**Table 1** Calculated onset temperature for Al(g) appearance and percent conversion of  $\text{Al}_2\text{O}_3$  to Al(g) by reactions with different initial  $\text{Al}_2\text{O}_3/\text{CH}_4$  molar ratios, and with  $\text{Al}_2\text{O}_3/3\text{C}$  (from Kruesi et al. 2011)

Reactants	Onset temperature (°C) for Al(g) production	Percent $\text{Al}_2\text{O}_3$ conversion to Al(g) at 2300°C
$\text{Al}_2\text{O}_3 + 2.5\text{CH}_4$	1342	46.4
$\text{Al}_2\text{O}_3 + 3\text{CH}_4$	1342	82.5
$\text{Al}_2\text{O}_3 + 4\text{CH}_4$	1342	87.0
$\text{Al}_2\text{O}_3 + 6\text{CH}_4$	1342	88.5
$\text{Al}_2\text{O}_3 + 3\text{CH}_4 + 10\text{Ar}$	1342	90.0
$\text{Al}_2\text{O}_3 + 3\text{CH}_4 + 20\text{Ar}$	1342	92.5
$\text{Al}_2\text{O}_3 + 4\text{CH}_4 + \text{H}_2\text{O}$	1581	83.0
$\text{Al}_2\text{O}_3 + 3\text{C}$	1943	69.3

### The System $\text{Al}_3\text{C}_4 + \text{Al}_4\text{CO}_4$

This combination shows that  $\text{Al}_2\text{CO}$  is the more stable compound below  $\sim 1500^\circ\text{C}$  and that the carbide is not stable in the presence of alumina. The reactions accounting for the formations of the aluminum oxycarbides are (Lihmann, Zambetakis, and Daire 1989; Fruehan, Li, and Cargin 2004)



in which Eq. (8) is the reverse of Eq. (4), and in which the mixture  $\text{Al}_2\text{O}_3 + \text{Al}_4\text{C}_3$  may form a liquid slag in the temperature region of  $1850\text{--}2160^\circ\text{C}$ , while Al-C may form a liquid alloy above  $2160^\circ\text{C}$ . The temperature dependence for the  $\text{Al}_3\text{C}_4 + \text{Al}_4\text{CO}_4$  system is shown in Figure 2. At above about  $1300^\circ\text{C}$ ,  $\text{Al}_2\text{CO}$  is converted to Al and C, and above  $2000^\circ\text{C}$  to  $\text{CO}(\text{g})$  and  $\text{Al}_2\text{O}(\text{g})$ .

### The System $\text{Al}_2\text{O}_3 + 2.5\text{CH}_4$

With an initial molar ratio  $\text{CH}_4/\text{Al}_2\text{O}_3 = 2.5$ , providing less than the required carbon component for the stoichiometry of Eq. (1), the predicted production of  $\text{Al}(\text{g})$  is accompanied by a substantial amount of the Al-suboxide,  $\text{Al}_2\text{O}(\text{g})$ , as shown in Figure 3, resulting in much decreased  $\text{Al}(\text{g})$  production (see Table 1).

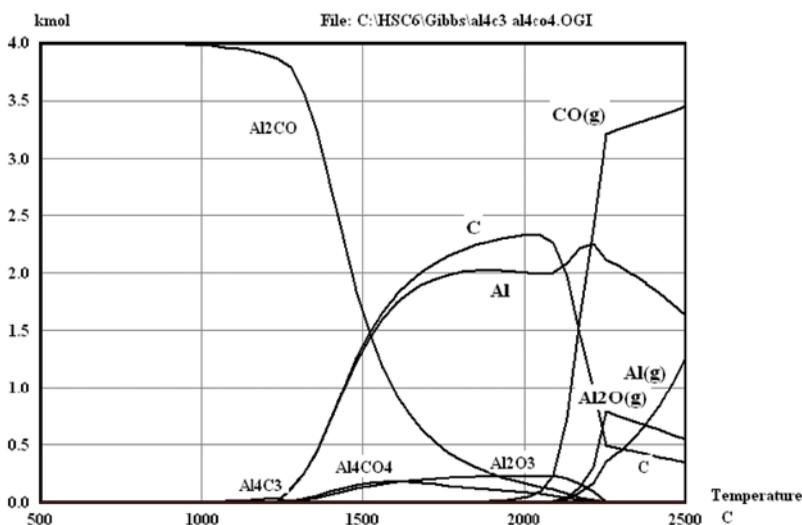


Figure 2 System  $\text{Al}_3\text{C}_4 + \text{Al}_4\text{CO}_4$  at 1 bar (color figure available online).

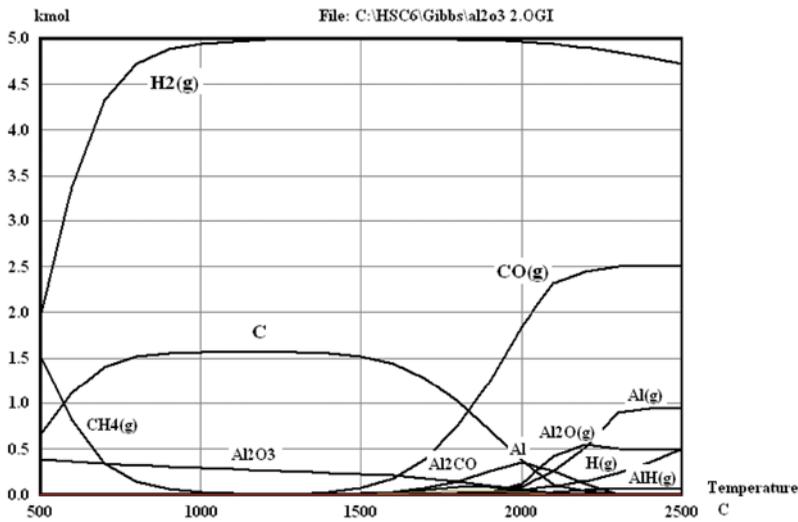


Figure 3 System  $\text{Al}_2\text{O}_3 + 2.5\text{CH}_4$  at 1 bar (color figure available online).

### The Systems $\text{Al}_2\text{O}_3 + 4\text{CH}_4$ and $\text{Al}_2\text{O}_3 + 6\text{CH}_4$

With an excess of  $\text{CH}_4$  relative to the stoichiometric  $\text{CH}_4/\text{Al}_2\text{O}_3$  ratio of Eq. (1), the equilibrium product compositions involve large amounts of  $\text{C}(\text{gr})$  accompanying the formation of  $\text{Al}(\text{g})$  (see Figures 4 and 5). The products are similar to those described in Figure 1 except that  $\text{C}_2\text{H}_2$  increases at higher temperatures.

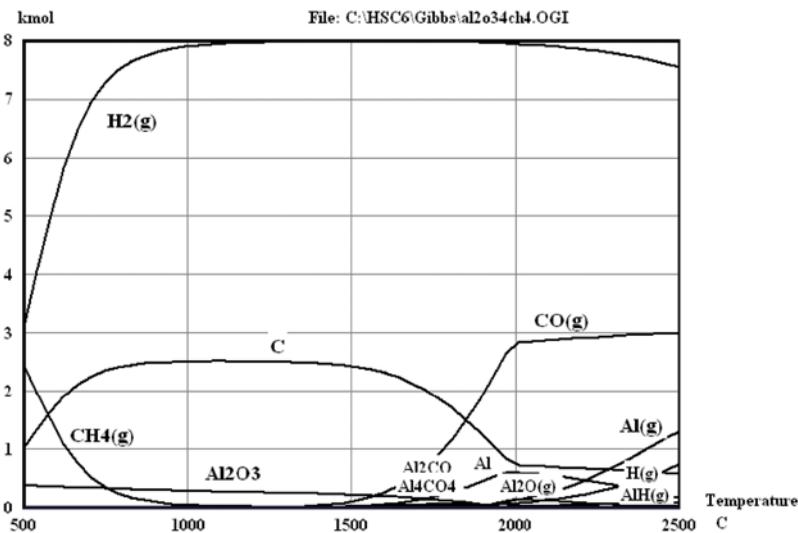


Figure 4 System  $\text{Al}_2\text{O}_3 + 4\text{CH}_4$  at 1 bar (color figure available online).

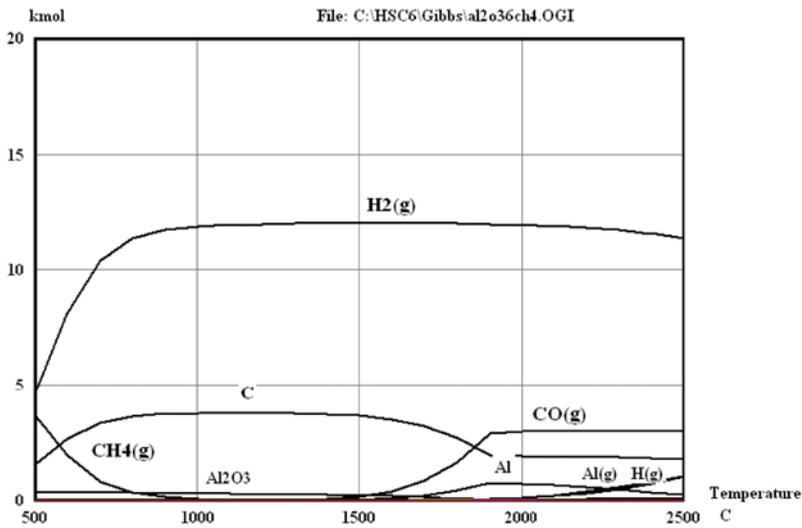


Figure 5 System  $\text{Al}_2\text{O}_3 + 6\text{CH}_4$  at 1 bar (color figure available online).

**The System  $\text{Al}_2\text{O}_3 + 4\text{CH}_4 + \text{H}_2\text{O}$**

Addition of 1 mol of  $\text{H}_2\text{O}$  results in “steam-reforming” of the excess of carbon in the system of  $\text{Al}_2\text{O}_3 + 4\text{CH}_4$ , with increased production of  $\text{H}_2$  and  $\text{CO}$ , but decreased production of  $\text{Al}(\text{g})$ , as shown in Figure 6, and listed in Table 1.

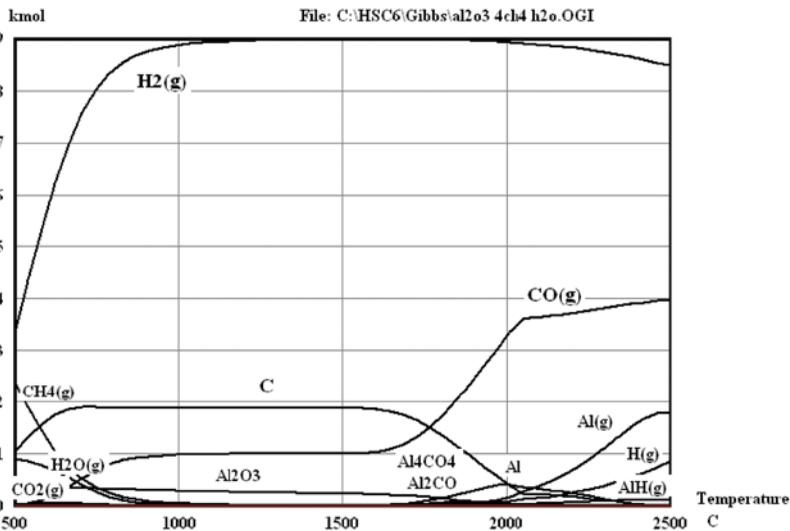


Figure 6 System  $\text{Al}_2\text{O}_3 + 4\text{CH}_4 + \text{H}_2\text{O}$  at 1 bar (color figure available online).

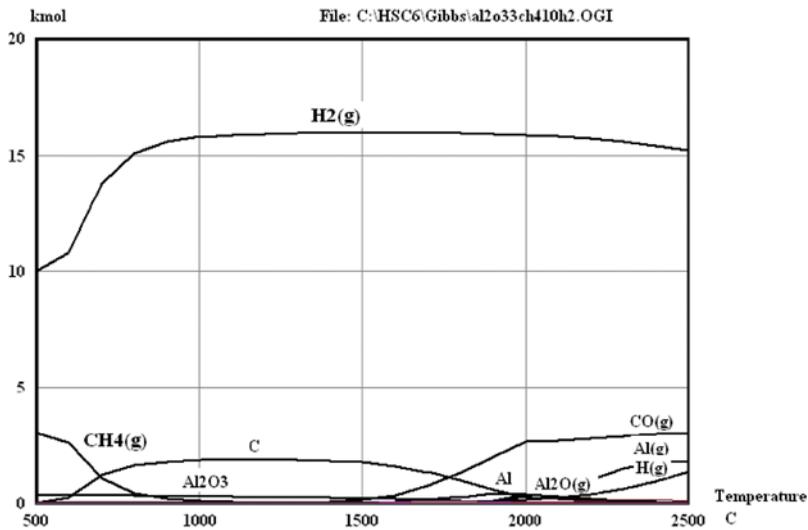


Figure 7 System  $\text{Al}_2\text{O}_3 + 3\text{CH}_4 + 10\text{Ar}$  at 1 bar (color figure available online).

### The System $\text{Al}_2\text{O}_3 + 3\text{CH}_4 + 10\text{Ar}$ and $\text{Al}_2\text{O}_3 + 3\text{CH}_4 + 20\text{Ar}$

Dilution of methane (3 volumes) by argon (10 or 20 volumes) results in significant calculated decreases in the production of  $\text{Al}_2\text{O}(\text{g})$ , and enhancement in the production of  $\text{Al}(\text{g})$  (Figures 7 and 8, in which the data for Ar are omitted for clarity of the figures) relative to those in the absence of argon (Figure 1), as described in Table 1.

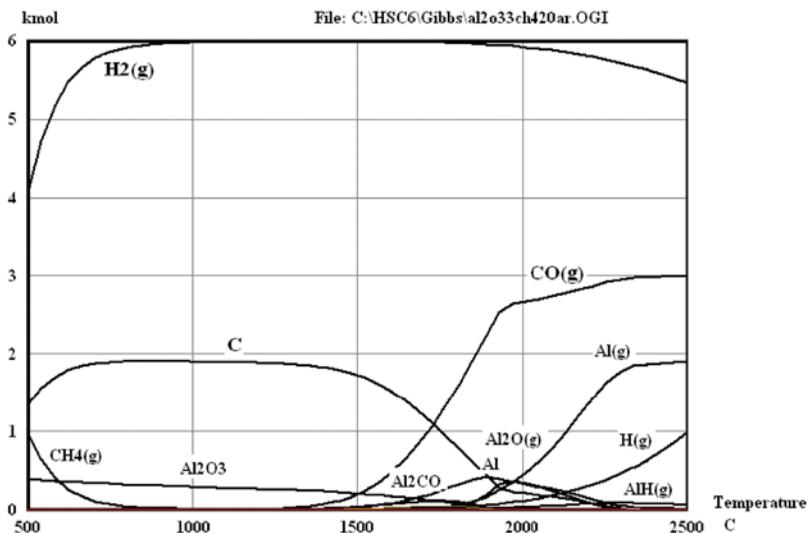


Figure 8 System  $\text{Al}_2\text{O}_3 + 3\text{CH}_4 + 20\text{Ar}$  at 1 bar (color figure available online).

## EXERGY EFFICIENCY

Exergy, or thermodynamic availability, represents the theoretical optimum work that can be performed as a result of the change of the state of a system to an equilibrium state (Halmann and Steinfeld 2006). The exergy efficiency is, here, represented by the ratio of maximal work output that can be extracted from the products, such as  $\Delta G$  of the complete oxidation of the products, to the enthalpy change of the reduction, and the heats of combustion (HHV) of the reactants (e.g.,  $\text{HHV}_{\text{CH}_4} = 890.8 \text{ kJ/mol}$ ), all calculated at  $25^\circ\text{C}$ . The reaction is assumed to occur as described in Eq. (3) for  $2500^\circ\text{C}$ , for which the enthalpy of the reaction is  $1978.9 \text{ kJ/mol Al}_2\text{O}_3$ , but disregarding the minor products  $\text{H(g)}$  and  $\text{Al}_2\text{O(g)}$ . The estimated exergy efficiency would be 75.9%.

## DISCUSSION

Above about  $700^\circ\text{C}$ , in the presence of alumina particles which provide nucleation sites,  $\text{CH}_4$  undergoes heterogeneous dissociation (cracking) to  $\text{H}_2$  and  $\text{C(gr)}$ . Above its melting point ( $2072^\circ\text{C}$ ),  $\text{Al}_2\text{O}_3$  will be liquid, and the reaction with  $\text{C(gr)}$  will be a liquid–solid process. However, up to about  $2200\text{--}2300^\circ\text{C}$ , the formation of  $\text{Al(g)}$  is accompanied by the byproducts  $\text{Al}_2\text{O(g)}$ , Al-oxycarbides, and  $\text{Al}_4\text{C}_3\text{(s)}$ . In the temperature range of  $2300\text{--}2500^\circ\text{C}$ , the carbothermic reduction of alumina should occur without these unwanted byproducts. The calculated onset of  $\text{Al(g)}$  appearance for most of the reaction systems studied above with  $\text{CH}_4$  as reducing agent is at  $1342^\circ\text{C}$ , while by reduction with solid carbon compounds the calculated onset of  $\text{Al(l)}$  is at  $1983^\circ\text{C}$  (Kruesi et al. 2011). As shown in Table 1, the presence of argon results in a marked increase in the calculated yield of conversion of alumina to aluminum, but its use would be prohibitive in a commercial application. The practical realization of the carbothermic reduction of alumina by methane to syngas and aluminum could be achieved by passing methane over alumina particles in a fluidized bed reactor. A similar process had been carried out for the combined calcination of  $\text{CaCO}_3$  and  $\text{CO}_2/\text{CH}_4$  reforming to lime and syngas in a particle flow reactor under concentrated solar radiation (Nikulshina, Halmann, and Steinfeld 2009). Process heat at the required temperatures could be supplied by concentrated solar energy (Steinfeld 1997; Murray 2001; Steinfeld and Palumbo 2001), by induction furnace heating, or by electric discharges (Rains and Kadlec 1970). Achievement of such high temperatures by solar energy will require secondary concentration, e.g., compound parabolic concentrators (Welford and Winston 1989). A mean solar concentration ratio exceeding 3000 suns ( $1 \text{ sun} = 1 \text{ kW/m}^2$ ) was applied to a 10 kW solar reactor for the thermal dissociation of  $\text{ZnO}$  at above  $1700^\circ\text{C}$  (Schunk et al. 2008; Schunk, Lipinski, and Steinfeld 2009). In a study of the direct solar water dissociation, a radiation concentration of the order of 10,000 was necessary to reach a temperature of  $2200^\circ\text{C}$  (Kogan 1998). A major advantage of carrying out the carbothermic reduction of alumina by the reaction with methane, relative to the solid–solid reaction (such as with charcoal, petcoke, or coke) would be the coproduction of syngas, useful for its conversion to liquid fuels or polymers, and with much decreased  $\text{CO}_2$  emissions. Another advantage of methane relative to charcoal would be the absence of the metal and nonmetal impurities

contained in plant-derived carbonaceous reactants. The main drawback would be the higher required reaction temperature, since it would be unfeasible to perform this reaction under vacuum. For the solid–solid carbothermic reduction of alumina, the necessary reaction temperature may be lowered even by 1000°C by operating under vacuum (Halmann, Frei, and Steinfeld 2011; Kruesi et al. 2011). To separate Al gas from H<sub>2</sub> and CO, one could apply the quenching device which was demonstrated to separate Zn from a gas mixture of Zn(g) and O<sub>2</sub>, and in which the product gases were quenched by water-cooled surfaces and by injection of cold Ar at cooling rates from 20,000 to 120,000 K/s, suppressing the formation of ZnO in the gas phase and at the walls, and removing the O<sub>2</sub> (Gstoehl et al. 2008). In an adaptation of such a device to the aluminum separation by condensation on a cool surface, the outgoing Ar, H<sub>2</sub>, and CO gas mixture could be cooled and pressurized to the condition required for methanol synthesis, passed over a methanol synthesis catalyst, while the argon would be recycled to the quenching device. Such an operation would also avoid the build-up of gas pressure in the reactor. An alternative approach for the separation of Al from the syngas could be by bubbling of the product mixture through liquid Al, which would require the absence of reaction of the CO with the liquid Al. Obviously, the reactor must be air-tight, both for safety reasons and to prevent reoxidation of aluminum. Experimental tests will be required to determine the kinetic rates of the pertinent reactions.

## ACKNOWLEDGMENTS

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## NOMENCLATURE

Al(g) gaseous Al  
C(gr) graphite

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