

Modeling of Catalyst Effect on the Reduction Rate Enhancement of Barium Sulfate by Methane and Developing Two Environmentally Friendly Processes

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Abstract

This article describes kinetic modeling of the reduction of barium sulfate by methane based on experimental data obtained by thermogravimetric technique. The conversion-time data have been interpreted by using the grain model for gas-solid reactions and the effect of catalyst on the kinetic parameters has been elucidated. It was found that zinc oxide acted as a fairly strong catalyst for the reaction, especially at higher temperatures. For example, at about 950°C the reaction rate constant was increased more than 8 times by using only 2 percent of zinc oxide. Orthogonal collocation method was used for solving coupled partial differential equations of gas-solid reaction. There is a good agreement between the experimental data and results obtained from simulation. This research offers a clean method for barium carbonate production with methane as a reducing agent, decreasing CO₂ emission significantly. Also, a new process for converting sulfur dioxide to elemental sulfur by a cyclic process involving barium sulfide and barium sulfate has been proposed.

Keywords: Modeling, Barium Sulfate, Methane Reduction, Catalyst, Zinc Oxide, Kinetic Study

1. Introduction

Reduction of barium sulfate (BaSO₄) to barium sulfide (BaS) is an important step in producing barium chemicals from barite (natural barium sulfate mineral). Barite ore is a basic starting material for manufacturing a variety of barium chemicals such as BaCO₃, Ba(OH)₂, Ba(NO₃)₂, Ba(HS)₂, BaO, etc. In the so-called “black- ash process”, the reduction of barite is carried out in a rotary kiln or in a fluidized bed at a high

temperature such as 1100-1200°C in the presence of reducing agents, mostly coal [1]. For example, barium carbonate can be produced industrially from barium sulfide solution by soda ash methods. In this method, the precipitation reaction in the aqueous media is as follows [1]:

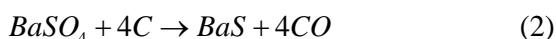


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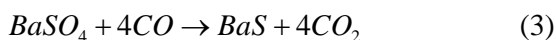
In the course of reduction, the prime reducing agent is carbon monoxide, which in turn is generated in situ by the reduction of carbon dioxide by carbon [2].

Studies on the kinetics of the reduction of barite are very limited, and only a few scientists have carried out mechanistic studies of the reduction of barite by carbon [3-8].

Recently, Gokaran et al. studied the non-isothermal carbothermic reduction of barite in the absence and presence of sodium vanadate catalyst [9]. All studies are unanimous of the opinion that initial reduction of barium sulfate with carbon takes place according to the following equation:



where both barium sulfate and carbon are in contact. The CO generated diffuses and reacts with barium sulfate, which is not in contact with carbon, as follows:



This CO₂ diffuses back into carbon to generate more CO according to the Boudouard reaction:



Thus, in the solid-state reduction of barium sulfate, CO is the gaseous intermediate.

Also, Pelovski et al. have studied the isothermal reduction of barite with Hydrogen; in this study the kinetic parameters of reaction were determined [10]. Recently, Sohn et al. have studied the

isothermal reduction of barium sulfate with Hydrogen in the presence and absence of nickel catalyst; also the kinetic parameters of the reaction were determined [11-12]. They developed a novel process for converting sulfur dioxide to elemental sulfur by a cyclic reaction scheme involving barium sulfide and barium sulfate. This process converts sulfur dioxide gas to elemental sulfur using barium sulfide as a reducing mediator, and the product sulfate is in turn reduced by hydrogen (or other suitable reducing agents) to regenerate the sulfide. The overall process begins with the sulfate as the starting material, and consists of the following two reactions in which the solids are repeatedly regenerated and used without net generation or consumption:



The reduction of an inorganic mineral with coal is not environmentally friendly. These reactions produce poisonous gases such as SO₂, CO and a large amount of CO₂, however reduction of these minerals with methane produces less CO₂ and no SO₂ or CO.

In countries such as Iran where coal is not abundant but large sources of natural gas are available, the use of methane or natural gas for ore reduction could be economically beneficial and environmentally favorable [13].

The goal of the present investigation is to investigate the reduction of barium sulfate by methane and to propose a kinetic model, both

in the presence and absence of zinc oxide as a catalyst.

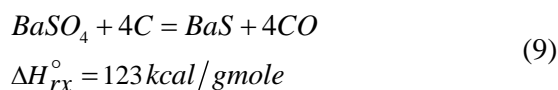
Also a new and cheap process for converting sulfur dioxide to elemental sulphur has been proposed in this study by the following reactions:



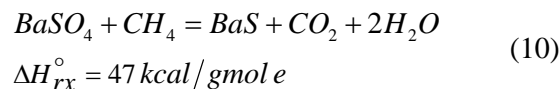
Schematic representation of the proposed thermochemical cycle of sulfur production using barium sulfide and barium sulfate is depicted in Fig. 1.

2. Thermodynamic Considerations

A common method for the barium sulfate reduction is based on high temperature reaction with coke. The enthalpy change and the overall reaction are as follows:



here, ΔH_{rx}° is the heat of reaction. Methane has a strong reducing capability and can react at lower temperature, viz:



Consider a general equation, as follows:

$$\sum \nu_R R = \sum \nu_P P \quad (11)$$

where R and P represent reactants and products, and ν_R and ν_P are the stoichiometric coefficients of reactants and products, respectively. The equilibrium constant of this reaction can be calculated from the following equation [14]:

$$\log K = \sum \nu_P \log K_{f,P} - \sum \nu_R \log K_{f,R} \quad (12)$$

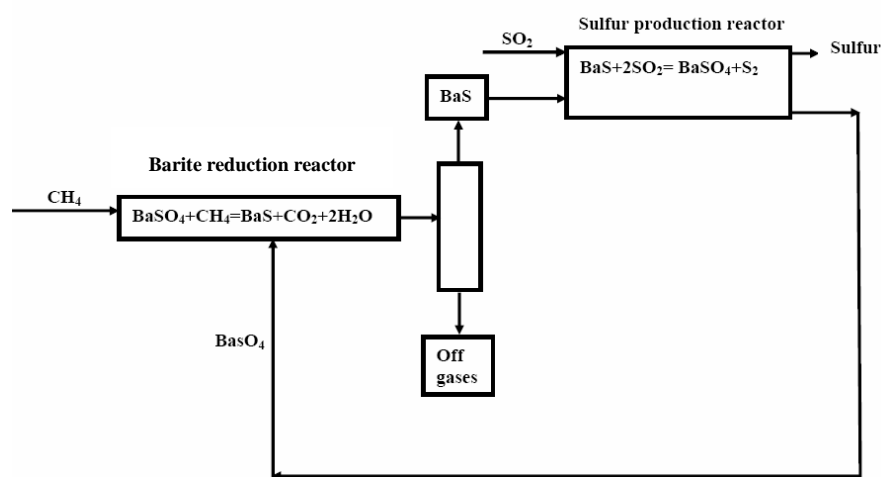


Figure 1. Schematic Flowsheet of cyclic process for sulfur production.

where K is the equilibrium constant of the reaction and $K_{f,R}$ and $K_{f,P}$ are equilibrium constants for the formation of reactants and products, respectively. From Eq. (12), the equilibrium constants of the reactions are computed and tabulated in Table 1, in which K_{CO} , K_{H_2} and K_{CH_4} are the equilibrium constants for the reactions in equation 3, 5 and 10 respectively and K_{Zn} is the equilibrium constant for the barium sulfate reduction by zinc vapour, explained in the results section. From Table 1, the greater reducing capability of the methane contrast with the carbon monoxide and hydrogen can be seen, therefore, the operating temperature can be decreased from about 1200 °C (black-ash process) to about 950°C for this process. This new process of barium sulfate reduction with methane has been registered as a patent [15]. Hydrogen can be applied as a reducing agent in the barite reduction process [11]. However, for industrial use, hydrogen is expensive in comparison with methane, and it is frequently produced by methane reforming.

3. Experimental setup

The thermogravimetric method was used to determine the kinetic parameters of the reaction; this method has been described in detail elsewhere [16]. The experimental setup is shown in Fig. 2. The vertical type high

capacity thermogravimeter (model TGH-1500) was obtained from Rheometric Scientific. The pellets were made using pure barium sulfate powder, and were then placed inside a platinum basket suspended from a string of a balance with an accuracy of 3 micrograms. The system was heated to the desired temperature under an inert gas stream such as helium or nitrogen (gas line 1). Initially, the isothermal period begins and after temperature stabilization, reducing gas (a mixture of CH₄/He through gas line 2) is introduced from the bottom of the instrument. The outlet gas stream leaves the system from the top and through a bubbler for slight positive pressure control.

The mole fraction of methane in the input gas mixture was fixed at about 0.4. The barium sulfate (BaSO₄) powder was supplied from Merck (Art. No. 1750) with a mean particle size of 0.22 micron. Figure 3. shows the scanning electron microscopy image of the starting barium sulfate powder. Also, zinc oxide (ZnO) powder was used from Merck (Art. No. 8849) with a mean particle size of 0.23 micron. The particles sizes were calculated using the average specific surface area of the pellet measured by BET analysis. Methane with 99.95% purity was supplied by the Air Products Company, while Helium and nitrogen with 99.999% purity were obtained from Messer Griesheim and Air Products Companies respectively.

Table 1. Equilibrium constants of barium sulfate reduction with different reducing agents.

T (°C)	K_{CH_4}	K_{CO}	K_{H_2}	K_{Zn}
800	9.1×10^7	7.0×10^5	5.3×10^5	7.7×10^{17}
900	6.3×10^8	2.0×10^5	5.8×10^5	1.6×10^{14}
1000	3.3×10^9	9.4×10^4	5.9×10^5	1.3×10^{11}

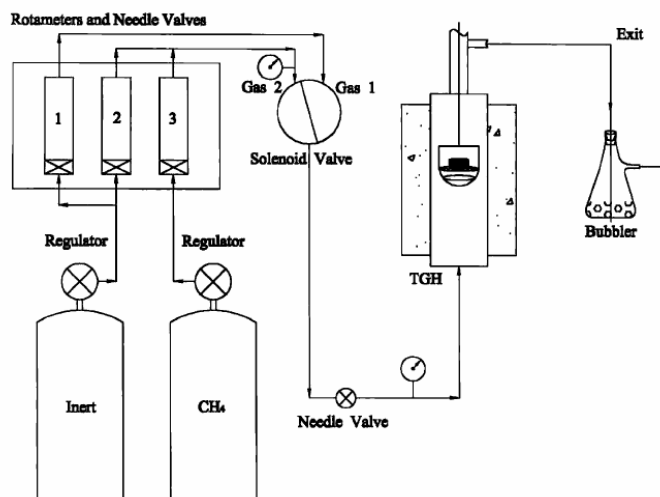


Figure 2. Flow diagram of system for kinetic study of this reaction

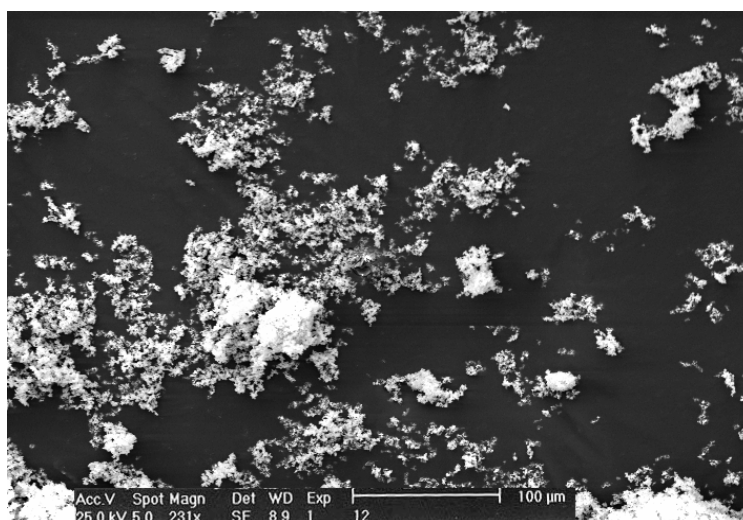


Figure 3. Scanning electron micrograph of the starting barium sulfate powder

Barium sulfate pellets were made by mechanical pressing of the powder in a pressing mold (3000 kg/cm^2). The diameter and thickness of the pellets are 7.2 mm and ca. 0.6 mm respectively, therefore the pellets can be assumed as slab-like. The reduction experiments were carried out at a

temperature range of 900-975°C under atmospheric pressure. Experiments were conducted with excessive reducing gas. Preliminary experiments showed that the reaction rate was not affected by the gas flow rate if the flow rate is greater than 120 ml/min, therefore a total gas flow rate was

maintained at 120 ml/min which means that external mass transfer resistance was negligible during the reaction. Two series of experiments were conducted, in the first series of experiments, pure barium sulfate pellets were used, and in the second series, the catalytic effect of zinc oxide on the reduction of barium sulfate was elucidated.

4. Mathematical modeling of experimental data

4.1. Assumptions and governing equations

The chemical reaction under consideration was expressed in Eq. (10), viz:

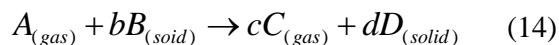


The “conversion” is defined as the weight loss of a pellet at a given time divided by the pellet weight when it is completely reduced, i.e., all of the oxygen atoms are liberated from it. Thus, the conversion-time curves can be obtained from the Thermogravimeter curves using the following relationship:

$$X(t) = (W_0 - W_t) / (W_0 M_{O_4} / M_{BaSO_4}) = 3.64(1 - W_t / W_0) \quad (13)$$

where W_t is the measured weight at time t , W_0 is the initial pellet weight, and M_{O_4} and M_{BaSO_4} are the molecular weights of liberated oxygen and barium sulfate, respectively.

The grain model introduced by Szekely et al. was used to analyze experimental data. This model is well described in the literature [17] and only a brief development is offered here. The barium sulfate-methane reaction may be represented by the following equation:



where b and d are stoichiometric coefficients of the solid reactant B and solid product D , respectively, and c is the stoichiometric coefficient of the product gas. The modelling is based upon the following assumption:

1. The pellet retains its initial size throughout the reaction
2. The reaction system is isothermal
3. The external mass transfer resistance is negligible
4. The intrinsic reaction rate is irreversible and first order with respect to methane concentration
5. The pseudo-steady approximation is valid.

The solid reactant is visualized as being composed of a large number of highly dense, spherical grains. Each of these grains reacts individually according to unreacted shrinking core model. However, in the overall pellet, the reaction occurs in a zone rather than at a sharply defined boundary. The reactant gas undergoes mass transfer from the bulk gas stream to the pellet surface. In order for the reaction to take place, the gas must diffuse from the surface to arrive at a sharp interface between the grain particle and the product layer. The schematic representation of the grain model was depicted in Fig 4.

The dimensionless governing equations of grain model for slab-like pellets with spherical grains are as follows [18]:

$$\frac{\partial^2 a}{\partial y^2} = \sigma^2 \cdot a \cdot r^{*2} \quad (15)$$

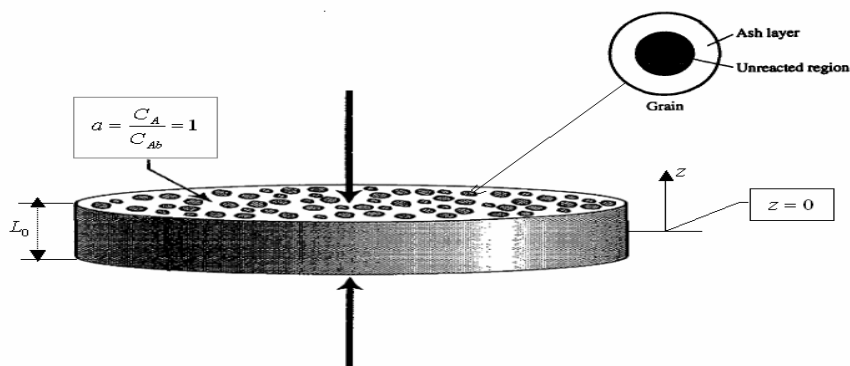


Figure 4. Schematic representation of the grain model.

$$\frac{\partial r^*}{\partial \theta_g} = -a \quad (16)$$

with the initial and boundary conditions:

$$\theta_g = 0, \quad r^* = 1 \quad (17)$$

$$y = 0, \quad \frac{\partial a}{\partial y} = 0 \quad (18)$$

$$y = 1, \quad a = 1 \quad (19)$$

where $a = C_A / C_{Ab}$ is the dimensionless gas concentration, C_A and C_{Ab} are the concentrations of reactant A in position y within a pellet and in bulk gas, $y = 2z / L_0$ is dimensionless position in the pellet, z is distance of each point from central cross section of the pellet parallel to the ends, L_0 is the thickness of the slab pellet, $r^* = r_{gc} / r_{g_0}$ is the dimensionless unreacted radius in the grain, r_{g_0} and r_{gc} are initial and unreacted core radius of grains, respectively, θ_g is the

dimensionless time for the grain model and is defined as follows:

$$\theta_g = \frac{bkC_{Ab}t}{\rho_B r_{g_0}} \quad (20)$$

where k is reaction rate constant, t is the time, ρ_B is the true molar density of solid reactant B. σ is the gas-solid reaction modulus and will be defined by Eq. (26).

The ratio of molar volume of the solid product to that of the solid reactant, Z_v , is defined as:

$$Z_v = \frac{d\rho_B M_D}{b\rho_D(1-\varepsilon_D)M_B} \quad (21)$$

where ε_D is the porosity of solid product, M and ρ are molecular weight and density, respectively, and b and d are stoichiometric coefficients of the solid reactant and solid product, respectively. Z_v is an indicator of the structural changes in the pellet during the course of the reduction reaction. The

Z_v value was calculated to be about 0.8 for reduction of barium sulfate to barium sulfide. Thus, the structural change can be ignored during the reaction [17].

4.2. Intrinsic rate constant calculation procedure

By using the equations of section 4.1 the governing equations can be solved and r^* is found in the time near zero as follows:

$$r^* = 1 - \frac{\text{Cosh}(\sigma \cdot y)}{\text{Cosh}(\sigma)} \cdot \theta_g \quad (22)$$

Extent of reaction or conversion for non-porous grains is defined as local conversion and is the ratio of mass of solid product produced at each time to mass of solid product if the grain converts to solid product completely; so for grains we have:

$$x = 1 - (r^*)^{F_g} \quad (23)$$

where x is the local conversion of the grains and F_g is the grain shape factor, which equals 1, 2 and 3 for slab-like, cylindrical and spherical grains, respectively. However, the conversion of the pellet (X) is defined as overall conversion and is calculated from local conversion integration over the pellet as follows:

$$X = \int_0^1 x \cdot dy = 1 - \int_0^1 (r^*)^3 \cdot dy \quad (24)$$

If the Eq. (22) was combined with Eq. (24) and then was integrated, the conversion of the pellet could be found at the time near zero, so the slope of conversion time curve in

the vicinity of zero can be shown to be as follows:

$$\left. \frac{dX}{dt} \right|_{t=0} = \frac{3b \cdot k \cdot C_{Ab}}{\rho_B \cdot r_{g0}} \cdot \frac{\tanh(\sigma)}{\sigma} \quad (25)$$

(Eq.(25) is only valid for initial reaction times, where the product layer is very thin.)

By ignoring the structural change of the pellet, the modulus of gas-solid reaction σ is defined for a flat pellet made from spherical grains as follows:

$$\sigma = \frac{L_0}{2} \sqrt{\frac{3 \cdot (1 - \varepsilon_0) k}{D_{eA} r_{g0}}} \quad (26)$$

where ε_0 is the initial pellet porosity which was estimated from the volume and weight of the pellet, D_{eA} is the effective diffusion coefficient of gaseous reactant A in the pellet. D_{eA} was estimated as follows [19]:

$$D_{eA} = \varepsilon_0^2 / \left(\frac{1}{D_{AM}} + \frac{1}{D_{AK}} \right) \quad (27)$$

where D_{AM} and D_{AK} are the molecular and Knudsen diffusivity of gaseous reactant A in the pellet, respectively. D_{AM} was evaluated using the Chapman-Enskog formula [20] and D_{AK} was calculated from the following equation [17]:

$$D_{AK} = \frac{4}{3} \left(\frac{8R_g T}{\pi M_A} \right)^{1/2} k_0 \quad (28)$$

where R_g is the gas constant, T is the absolute temperature, M_A is the molecular

weight of the gaseous reactant and k_0 was calculated from the 'dusty gas model' of Mason et al [21] as follows:

$$\frac{1}{k_0} = \left(\frac{128}{9} \right) n_d r_g^2 \left(1 + \frac{\pi}{8} \right) \quad (29)$$

It should be noted that n_d , the number of solid grains per unit volume of porous solid, was calculated as follows:

$$n_d = \frac{3(1 - \varepsilon_0)}{4\pi r_g^3} \quad (30)$$

By combining Eq.(25) with Eq. (26), there is only one unknown parameter (k) that can be computed by solving the nonlinear equation.

4.3. Extent of reaction calculation

For determining the extent of the reaction, the diffusion equation (Eq.15) and reaction equation (Eq. 16) must be solved simultaneously; this is a mixed boundary value problem. These coupled partial differential equations are tedious to solve, and many works have been done to solve them. Dudukovic et al. [22] used integral transformation to reduce the coupled partial differential equations to a two-point non-linear boundary value problem in space, and an efficient technology was used to solve this boundary value problem using three and eight-point orthogonal collocation. This method is clearly described in the literature and only a brief explanation is offered here [22].

First of all, it is convenient to introduce the cumulative gas concentration by applying integral transformation as follows:

$$Y = \int_0^{\theta_g} a.d\theta_g \quad (31)$$

here, Y is cumulative gas concentration, and also in orthogonal collocation method; gradient operator and laplacian operator could be replaced as follows [23]:

$$\frac{\partial Y^n}{\partial y} = \sum_{j=1}^{n+1} A_{ij} Y_j \quad (32)$$

$$\nabla^2 Y^n = \sum_{j=1}^{n+1} B_{ij} Y_j \quad (33)$$

In addition, the following integral could be calculated precisely as:

$$\int_0^1 f(x) x^2 dx = \sum_{j=1}^{n+1} W_j^{(n)} f(x_j) \quad (34)$$

In which $A_{i,j}$, $B_{i,j}$ and W_j are matrix coefficients for the 8 point orthogonal collocation method. These coefficients were defined by Dudukovic et al.[22] in which n is the collocation point number and the point (1 + n th) represents the surface of the pellet. In this study we neglected the external mass transfer resistance, thus the value of Y is known at the surface of the pellet as.

$$Y_{n+1} = \theta_g \quad (35)$$

By combining the above mentioned equations with the governing equations and then integrating will result in the final equation as follows:

$$\frac{\partial^2 Y}{\partial y^2} - \frac{\sigma^2}{3} [r^{*3} - 1] = 0 \quad (36)$$

The boundary conditions are:

$$y = 0, \frac{\partial Y}{\partial y} = 0 \quad (37)$$

$$y = 1, Y = 1 \quad (38)$$

Combining and rearranging the governing equations with the above-mentioned equations will produce the following matrix equations:

$$\sum_{\substack{j=1 \\ i \neq j}}^{n+1} B_{ij} Y_j + \frac{\sigma^2}{3} [r_i^{*3} - 1] = 0 \quad i = 1, 2, 3, \dots, n+1 \quad (39)$$

By solving the matrix equations the final conversion of the pellet will be calculated using Eq. 23, as follows:

$$X = 1 - 3 \int_0^1 r^{*3} dy = 1 - 3 \sum_{j=1}^{n+1} W_j r_j^{*3} \quad (40)$$

5. Results and Discussion

The zinc oxide was already found to substantially enhance the rate of the methane reduction of lead oxide [24], for this reason its effect on the reduction of barium sulfate was elucidated in this work.

The transient weight loss of the barium sulfate pellet vs. time in the thermogravimeter during the reaction was shown in Fig. 5 at 975°C and methane concentration of 0.4-mole fraction.

The substantial effect of catalyst on barium sulfate reduction can be seen from the thermogravimetric curves.

The reaction rate constants can be calculated for different temperatures using the procedure presented in section 4.2. The numerical values of the reaction rate constants at different temperatures and for three typical cases (with 1% and 2% catalyst and noncatalytic) are presented in Table 2.

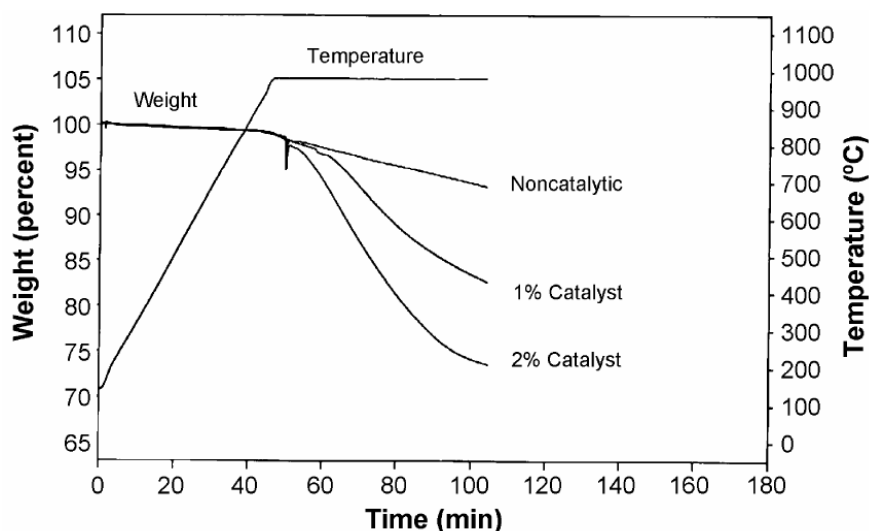
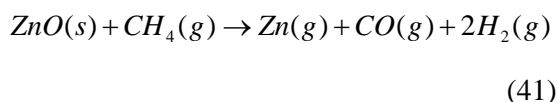


Figure 5. Weight change curve at 975°C versus time in three modes

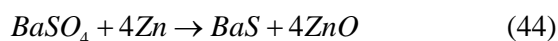
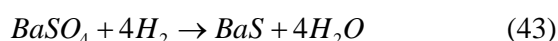
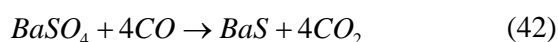
Table 2. Rate Constants ($k(cm/s)$) for the Reduction of Barium sulfate by Methane under Catalytic and Noncatalytic condition

T (°C)	Noncatalytic	1% catalyst	2% catalyst
900	1.11×10^{-7}	2.84×10^{-7}	5.97×10^{-7}
925	3.40×10^{-7}	1.42×10^{-6}	2.03×10^{-6}
950	5.49×10^{-7}	1.80×10^{-6}	4.68×10^{-6}
975	9.44×10^{-7}	5.36×10^{-6}	7.24×10^{-6}

By comparing the results in Table 2, it is clear that zinc oxide has considerable influence in enhancing the value of k , and hence the reactivity of methane with $BaSO_4$. Like the reduction of lead oxide (PbO) with methane [24], this effect may be due to the reduction of zinc oxide by methane as the following reaction [25]:



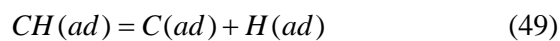
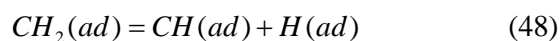
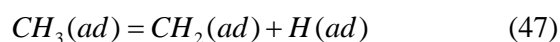
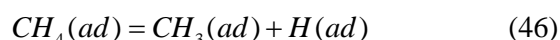
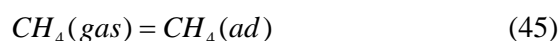
All of the produced gases by reaction (41) are reducing agents and can react in situ with barium sulfate and cause the following reactions simultaneously [9,11,26]:



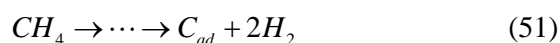
Reactions (2) and (4) have been comprehensively studied already [9, 11]. Table 1 shows that the reaction (42) is thermodynamically feasible and the capability of zinc vapor in barium sulfate reduction is even higher than the methane.

Furthermore, pores development in a solid matrix due to zinc volatility increases the reaction surface area. Also, zinc oxide plays a beneficial role in increasing the number of active sites generated in the barium sulfate matrix.

In metal oxide reduces reactions with methane, while the reduction process starts with the adsorption of methane on the active sites of the oxide surface and its decomposition, as described by the following reactions [27]:



The overall reaction of methane adsorption and cracking may be presented as:



In which C_{ad} represents active carbon species adsorbed on the solid surface. When the methanothermal reaction temperature is higher than 1000°C , methane cracking can be a severe problem. The overall reaction of methane cracking may be presented as follows:



In which C_{gr} represents deposited carbon on a solid surface. In this study the temperature is low, thus carbon deposition is not a problem.

Fig. 6 shows the X-ray diffraction pattern of the product of the completely reduced barium sulfate catalyzed by 2 percent of zinc oxide using methane at a temperature of 950°C . Only barium sulfide was detected by XRD.

The zinc or zinc oxide was not seen in the XRD pattern, and there is no carbide or oxide phase. It is clear that when barium sulfate reacts with methane, the solid product is barium sulfide.

The Arrhenius equation is obtained by considering the temperature effect on the reaction rate as follows:

$$k = k' e^{-\frac{E_a}{R_s T}} \quad (53)$$

where k' is the frequency factor and E_a is the apparent activation energy.

By using the procedure introduced in section 4.3, the extent of reaction (X) was calculated and compared with the grain model. The data presented in Figs. 7-9 indicate quite good consistency between the kinetic grain model and the experimental data.

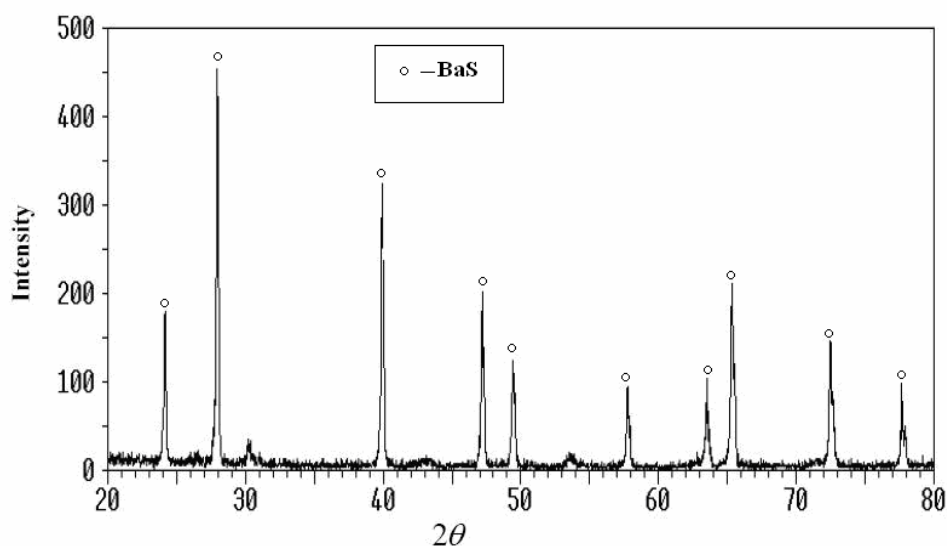


Figure 6. XRD pattern of product prepared at 950°C and catalyzed by 2% of zinc oxide

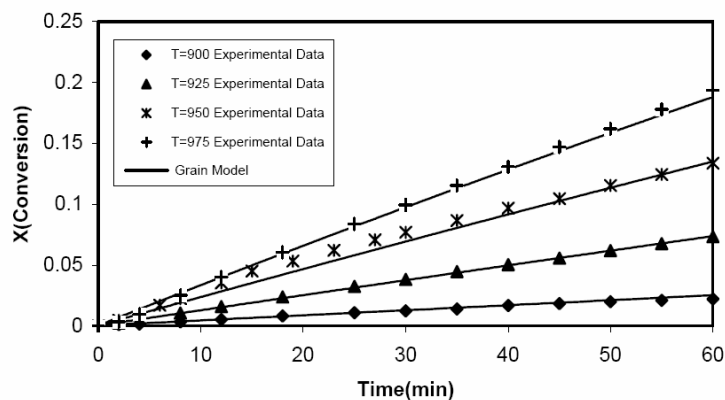


Figure 7. Reduction curves in grain model (lines) in comparison with experimental data (symbols) at different temperatures for noncatalytic mode.

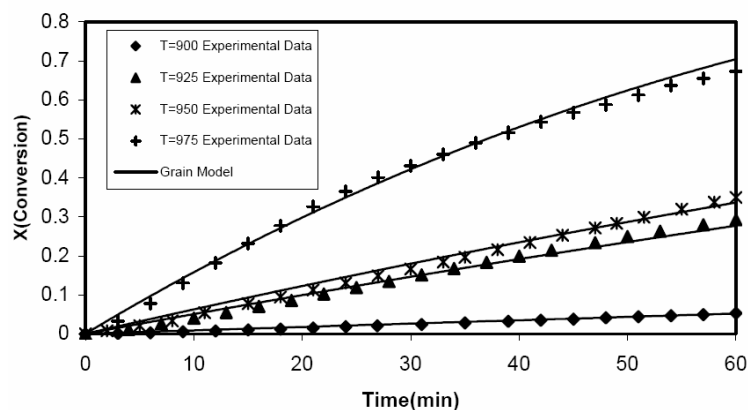


Figure 8. Reduction curves in grain model (lines) in comparison with experimental data (symbols) at different temperatures for 1% catalyst mode.

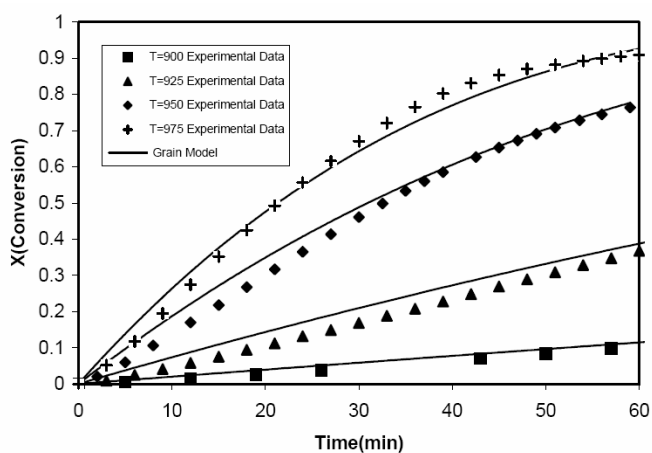


Figure 9. Reduction curves in grain model (lines) in comparison with experimental data (symbols) at different temperatures for 2% catalyst mode.

The average activation energy for the barium sulfate reduction is found to be ca. 96 kcal/gmol. It is useful to make a comparison with activation energy data of barium sulfate reduction reactions by other compounds reduction by methane given in the literature; for example, the activation energy for reduction of ZnO to Zn with methane at a temperature range of 840 to 930 °C is found to be 67.09 kcal/gmole [25], also, the activation energy for reduction of Fe₂O₃ to Fe with methane is 52.7 kcal/gmole at a temperature range of 875 to 950 °C [28], the activation energy for the nickel oxide reduction by methane is ca. 64 kcal/gmole at a temperature range of 600 to 725 °C [29]. Finally, activation energy for the cobalt oxide reduction with methane has been found to be 37 kcal/gmole at a temperature range of 800 to 950 °C [30]. Thus, the value reported in this article for the reduction of barium sulfate with methane is within the same order of magnitude as the values for the reduction of ZnO, Fe₂O₃, NiO and CoO with methane.

6. Conclusions

In this research, kinetics of barium sulfate reduction with methane was studied by thermogravimetry and the solid products analyzed by XRD. Then, from initial conversion-time slopes, the kinetic parameters of this reaction were calculated in the presence and absence of catalyst at a temperature range of 900-975°C. The extent of reaction (X) was calculated by orthogonal collocation method and compared with the experimental data. The kinetic grain model resulted in good agreement with the experimental data. This method reduces greenhouse gas emission (CO₂), and produced no SO₂ or CO as in the black ash process. Another important result of this work is the decrease in the operating

temperature (from 1200 to 950°C) and in the heat of the reaction (from 123 kcal/gmole to 47 kcal/gmole) with respect to the usual coal-based reduction method. Moreover, by using methane which is introduced by the ash and sulfur of the coal in the black-ash process, the impurities in the product can be decreased significantly. Also, in this method one mole of methane can perform the duty of 4 moles of carbon as a reducing agent. This research offers a clean method for barium carbonate production with methane as a reducing agent, which decrease CO₂ emissions significantly. A new process for converting sulfur dioxide to elemental sulfur by a cyclic process involving barium sulfide and barium sulfate has been proposed as well.

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