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Thermal ignition of coal powders in the presence of natural gas, oxygen and chemically active additives

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At 650–750 °C, a coal powder–gas mixture containing stoichiometric amounts of natural gas and air does not burn over a surface coated with coal powder due to the inhibiting effect of gases evolving during the thermal annealing of coal powder. The ignition of the powder–gas mixture can be promoted with small amounts of a chemically active additive (*e.g.*, dichlorosilane).

Dust explosions are dangerous for processing and mining industries, when the formation of suspensions of combustible particles in a gas containing an oxidant occurs. Experimental investigations showed that the probability of dust explosion increases if even minor amounts of a combustible component were contained in the powder–gas mixture (hybrid PGM).[1] According to Seplyarskii *et al.*,[2] the minimum energy of ignition of hybrid PGM could be decreased by a factor of 20–30 with the addition of 2–3% methane. Note that the conditions are typical of coalmines, where combustibles, coal powder and methane can occur simultaneously. This brings even a greater hazard in closed volumes, *e.g.*, mines. Therefore, the investigation of the ignition of coal hybrid PGMs containing natural gas and oxygen at room and higher temperatures is highly important.

We have shown recently[3] that a stoichiometric mixture of natural gas (NG) with oxygen (O_2) self-ignites over coal coating much worse than combustible volatiles evolving from coal coating in pure oxygen. The volatiles had an inhibiting effect on NG combustion. Thus, under certain conditions, coal powder may be the major source of danger because at higher temperatures it can self-ignite before the self-ignition of an NG–O_2 mixture.

The aim of this work was to study the influence of different coal powders as hybrid PGMs on the ignition of NG and O_2 mixtures. The other objective was to elucidate the possibility of controlling the ignition of hybrid PGM containing coal powder and NG in O_2 by means of small amounts of chemically active additives.

Experiments were carried out at a total pressure of 73 Torr at 685 °C in a heated quartz cylinder 3.6 cm in diameter and 25 cm in length. Coal hybrid PGM in the reactor was produced in the setup shown in Figure 1. Coal powder (0.2 g, particle size of ~90 μm) was poured into the quartz trough placed in the reactor at its inlet, and the reactor was pumped to 10^{-2} Torr. Then, the coal powder was thrown into evacuated reactor with a sharp stream of the test gas mixture from a buffer volume so that the total pressure in the reactor was 73 Torr. Ignition was recorded by means of a Casio Exilim F1 Pro colour high-speed digital camera (1200 frames s^{-1}). It was shown that hybrid PGM obtained as described above occurred in the reactor volume at 680 K for no less than 2 s. To be certain that coal particles remain in PGM the particle cloud was imaged using a horizontal sheet of He–Ne laser light ($l = 632.8$ nm) formed by means of a cylindrical lens along with camera recording (not shown in Figure 1) as described previously.[4] Therefore, in our experiments at induction periods $\tau < 2$ s, coal particles remained in the mixture. Emission spectra of initiated ignition were recorded with a spectrograph with crossed dispersion equipped with a CCD camera sensitive over the range of 420–900 nm. The spectra were analyzed using the AmLab Hesperus 3.0 beta program package. NG contained 98% CH_4, 2% propane and butane. The following different types of coals of particle size < 90 μm (the sieve retained oversize powder) were used: high volatile steam coal (HV, ~38% volatiles, GOST 10101-79), coking coal (C, ~17% volatiles, GOST 25543-88) and anthracite (A, ~8% volatiles, GOST 25543-88). The powder of coking coal with a particle size of < 60 μm was used in an experiment. The reactor surface was coated with coal powder in a series of experiments. For coating, the suspension of coal powder (0.2 g) in ethanol (2 ml) was placed in the reactor and rotated under pumping to remove the liquid.

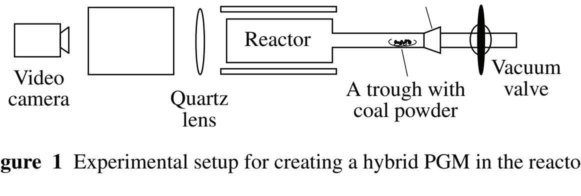

Figure 1 Experimental setup for creating a hybrid PGM in the reactor.

The measured τ of self-ignition of 33% NG in O_2 (73 Torr, 685 °C) in the absence of PGM was considered as a control point. The value of τ was 48±2 s over a quartz surface freshly treated with HF.

First, the reactor surface was coated with coal A powder. When HV coal powder was thrown into the heated reactor with a stream of pure O_2, intense self-ignition was observed in 0.5 s. However, the injection of the powder with 33% NG + O_2 (stoichiometric) into the reactor resulted only in weak luminescence. In the emission spectrum of intense ignition, the intense C_2 emission band A^3P_g–X^3P_u (transitions 1–0, 0–0)[5,6] was observed along with the emission of CH radicals ($A^1\Delta$–$X^2\Pi$)[5] at 431 nm (Figure 2).[3] The spectrum shows that volatiles evolving from coal powder burn in oxygen yielding excited C_2 radicals; therefore, the volatiles are probably hydrocarbons.[5] These volatiles can provide the inhibiting effect of coal powder on the combustion of NG.

Indeed, as is seen in Figure 2(*a*), in self-ignition of 33% NG + O_2 in A powder coated and thermally treated reactor,[3] a band system in the red area is observed along with the band systems of C_2 and CH radicals, as well as atomic emission of alkali metals (Li, Na, K and Rb[7]). The red system is missing in

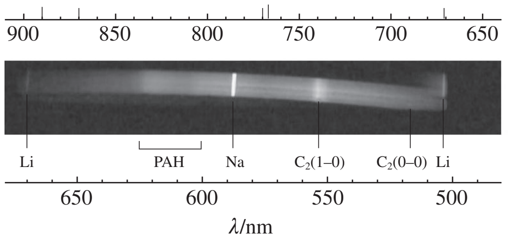

Figure 2 Emission spectra of C_2 radicals (A^3P_g–X^3P_u) at 557 nm in the reaction of oxygen (73 Torr) with HV coal powder at 685 °C.

the emission spectrum of self-ignition of 33% $NG + O_2$ over quartz surface under the same conditions (685 °C, 73 Torr). To check our assumption on the pathway of red system formation, 5 Torr of perfluorodecaline ($C_{10}F_{18}$) was added to the mixture of 33% $NG + O_2$ to a total pressure of 73 Torr. The emission spectrum of self-ignition of the mixture is shown in Figure 3(*b*). Since HF (3–0) emission[5] is observed in the spectrum, the molecules can be produced only if F atoms are removed from $C_{10}F_{18}$; in this case, unsaturated C–C bonds are generated in the molecule, *i.e.* the molecule becomes aromatic, as is shown in Figure 3. Therefore, in the process the formation of a polycyclic aromatic hydrocarbon (PAH) is simulated. As is seen in Figure 3, red emission bands in spectrum *b* are observed over the same interval of wavelengths (600–630 nm) as in spectrum *a*. In addition, spectrum *b* over this spectral interval is almost similar to emission of PAHs observed elsewhere.[6] Therefore, it may be suggested that the volatiles evolving from coal powder contain PAHs. It is of interest to try some PAHs with appropriate vapour pressure as inhibitors in further experiments.

It was shown that, if the hybrid PGM was formed with the stream of 9% $NG + O_2$ and any one of types of coal powder, the luminescence in the coal A coated reactor was also weak; *i.e.*, ignition was missing. However, if the C powder with a particle size of < 60 μm was injected into the reactor with 9% $NG + O_2$, the ignition was observed. It means that that the conditions of the self-ignition limit of coal hybrid PGM depend strongly on both NG concentration in the mixture and the coal particle size.

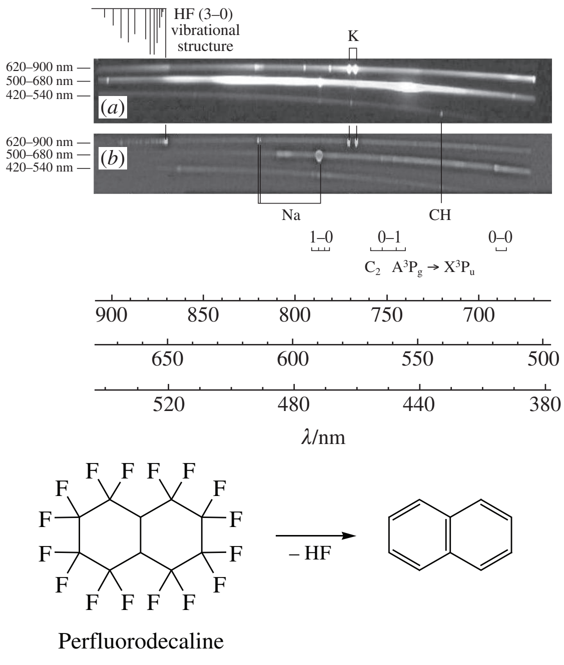

Figure 3 Emission spectra of (*a*) self-ignition of 33% $NG + O_2$ in A powder coated and thermally treated reactor (73 Torr, 685 °C) and (*b*) self-ignition of 33% $NG + O_2 + C_{10}F_{18}$ (5 Torr) over a quartz surface under the same conditions (685 °C, 73 Torr).

Notice that video recording of all intense ignitions of hybrid PGM under our conditions showed that the ignition of gas in the reactor volume is always preceded by the ignition of coal powder (multiple bright sparks in the reactor).

However, the stream of 4.5% $NG + O_2$ in coal A coated reactor gave an intense ignition, but only if C and A powders were used to form hybrid PGM; in this case, A powder provided the most intense flash. Therefore, the smaller the amount of volatiles in the powder, the more intense the ignition of the hybrid PGM with 4.5% $NG + O_2$. Note that the gas mixture (4.5% $NG + O_2$) was beyond a self-ignition area under our conditions (685 °C, 73 Torr), *i.e.*, coal powder combustion promotes ignition of the gas mixture.

The second series of measurements was performed over a quartz surface freshly treated with HF. When coal C powder was thrown into the reactor with the mixture of 9% $NG + O_2$ intense ignition was observed, though there was no ignition over coal A treated surface (see above). It means in accordance with our previous measurements[3] that coal surface (as distinct from HF treated quartz) under thermal annealing evolves an inhibitor, which prevents ignition of the mixture (9% $NG + O_2$) in case of the reactor surface coated with coal powder.

Note that the rate of heterogeneous termination of active centres of combustion must increase in the presence of coal hybrid PGM in the reactor at the cost of increase of total surface area. The factor also interferes with ignition. However, previously,[3] we showed by the example of H_2 oxidation that with increasing temperature, the value of lower limit of self-ignition over coal coating exceeds the diffusive one, *i.e.*, the volatiles evolving from heated coal powder provide an inhibiting effect on $H_2 + O_2$ combustion. Moreover, thermal annealing of coal powder deposited on reactor walls causes the self-ignition of a stoichiometric $NG + O_2$ mixture,[3] though thermally annealed surface is more chemically active,[7] and it exhibits an opposite action. The inhibiting effect of coal powder on NG combustion is connected predominantly with volatiles evolving from heated coal powder rather than with the ability of coal powder surface to terminate reaction chains.

The following series of experiments was aimed at establishing the possibility of controlling the ignition of hybrid PGM containing coal powder and NG by means of small amounts of chemically active additives. It is known that tetrachloromethane acts as an inhibitor on self-ignition and combustion of methane–air flames;[8,9] dichlorosilane (SiH_2Cl_2) reacts with oxygen at lower concentrations and temperatures as compared to methane.[7] Therefore, the additives of CCl_4 (possible inhibitor) and SiH_2Cl_2 (possible promoter) were used in the experiments. It was shown that, if the hybrid PGM of any type of coal powder was formed with the stream of the mixture (2–3.5%) $CCl_4 + O_2$, an intense flash was observed in the reactor. It means that CCl_4 additives do not affect the ignition of volatiles evolving from coal powder as inhibitor under our conditions.

In experiments with SiH_2Cl_2 additives, the induction period of self-ignition of 3% SiH_2Cl_2 to 33% $NG + O_2$ in the absence of PGM was at first determined. It was 13 s at 695 °C and 73 Torr. When HV powder was injected into the reactor with the stream of 33% $NG + O_2 + 3\%\ SiH_2Cl_2$, the intense ignition was observed in 1 s. Note that we managed to ignite HV powder only with pure O_2, though the hybrid PGM containing 33% $NG + O_2$ without SiH_2Cl_2 and coal powders of each type could not be ignited anyway. It points to the fact that the ignition of coal hybrid PGM containing NG is promoted with small dichlorosilane additives.

However, after pumping out the reactor, the next injection of the coal powder with 33% $NG + O_2 + 3\%\ SiH_2Cl_2$ to form hybrid PGM provided less intense ignition. It also means in accordance with our previous measurements[3] that the coal surface under annealing evolves a certain inhibitor, which prevents the ignition of the mixture.

Therefore, in the absence of hot walls coated with coal powder (*i.e.*, if the hot surface does not evolve the inhibitor), even HV powder could be ignited in the presence of a promoter. The ignition of hybrid PGM can be affected by means of a small amount of a promoter; therefore, it is possible to work out a suitable additive acting as an inhibitor.

In summary, the main features of the ignition of coal hybrid PGMs at higher temperatures are the following:

– HV powder cannot ignite NG (4.5–33%) + O_2 mixtures, though it ignites in pure O_2.

– The state of the reactor surface markedly influences the ignition of hybrid PGMs; the hot surface evolves an effective inhibitor of methane combustion, probably, PAH.

– The degree of dispersion of coal powder is a factor affecting the ignition of hybrid PGM.

– The ignition of hybrid PGMs could be promoted with small amounts of a chemically active additive (*e.g.*, dichlorosilane).

– In the combustion of the hybrid PGM, the ignition of a gas in the reactor volume can be preceded by the ignition of coal powder.

It follows from the results obtained that the gases evolving during the thermal annealing of coal powder have an inhibiting effect on the combustion of natural gas; therefore, chemical methods can be used to control the ignition of hybrid PGM containing NG.

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