

The impact of the distributions of surface oxides and their migration on characterization of the heterogeneous carbon–oxygen reaction

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Abstract

A study was undertaken to characterize the impact of the heterogeneity and migration of surface oxides on the char oxidation process. The char employed in the study was subjected to a series of kinetics-limited oxidation tests in a pressurized thermogravimetric analyzer (PTGA). Temperature-programmed desorption and BET-CO₂ gas adsorption tests were also performed in order to characterize surface oxide complexes and specific surface areas. In agreement with other studies, the experiments indicated that the surface-oxide populations may be characterized in terms of a distribution of desorption activation energies and that migration of the surface oxide complexes is significant. A heterogeneous reaction mechanism was developed to account for the observed rates of O₂ adsorption, CO and CO₂ desorption, and surface-oxide accumulation and was used in a numerical algorithm that modeled the PTGA reaction environment. Surface species were characterized by activation-energy-based distributions; allowance was made for the impact of surface area evolution on surface species concentrations. Analysis of calculated results indicate that a quasi-steady surface area assumption tends to underpredict surface species concentrations, especially at late conversions, but can overpredict these concentrations at early conversions. Calculated results also indicate that using less than five sites to approximate activation energy distributions yields results that are inconsistent with oxidation behaviors that are based on the full distributions.

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1. Introduction

In 2004, about 6.1 billion short tons of coal were consumed worldwide, which represented about 26%

of the total energy consumed in the world [1]. Coal is the most abundant of all fossil fuels. It is the source for roughly one-third of the electric power produced in the world. It is used to generate over half of the electricity consumed in the United States, which has over 200 years of coal reserves at current consumption rates. Coal will play a dominant role in electric power generation in the United States for at least the

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Nomenclature

E	activation energy; desorption energy, kJ/mol	$\hat{R}_{S,j}$	molar production rate of species j per unit surface area of char, mol/s m ²
$E_{des,l}$	desorption energy of adsorbed species populating the l th subrange, . . kJ/mol	S	carbon site density, sites/m ² (taken as 6.5×10^{19} sites/m ²)
$[j]$	surface concentration of species j , mol/m ²	S_{gc}	specific char surface area, m ² /g
k_i	reaction rate coefficient for reaction i , with units consistent with surface concentrations in mol/m ² -surface and gas-phase concentrations in mol/m ³ -particle volume	S_{tot}	total char surface area, m ²
L	number of distinct sites considered in the distribution of desorption energies	T	temperature, K
\hat{M}_C	atomic mass of carbon, kg/kmol	T_{stp}	the standard calibration temperature, K
\hat{M}_O	atomic mass of oxygen, kg/kmol	t	time, s
$m_C(t)$	instantaneous mass of the carbonaceous char sample, kg	x_C	char conversion
$m_O(t)$	instantaneous mass of adsorbed oxygen, kg	y_j	mole fraction of species j in the PTGA exhaust gas
$m_{tot}(t)$	instantaneous total mass, kg	<i>Greek symbols</i>	
N	total moles of gas, mol	η_j	number of carbon sites that one molecule of species j occupies
\dot{N}	molar flow rate, mol/s	θ_j	fraction of carbon sites occupied by species j
N_{AV}	Avogadro's number, molecules/mol	$v_{i,j}$	reaction coefficient for species j as a reactant in the i th reaction
N_j	total moles of species j , mol	$v'_{i,j}$	reaction coefficient for species j as a product in the i th reaction
P_{stp}	the standard calibration pressure, . . . Pa	$\Phi(E_{des,l})$	fractional contribution of the l th sub-population of desorption energies
Q_{stp}	standard volumetric flow rate exiting the PTGA reaction chamber, m ³ /s	$\phi(E_{des})$	true distribution of oxygen complexes on the char surface
\Re	universal gas constant, J/mol K	φ	pore structure parameter
$\hat{R}_{R,i}$	molar reaction rate of reaction i per unit surface area of char, mol/s m ²	$\Psi(E_{des,l})$	integral of $\psi(E_{des})$ over the energy range of the l th subpopulation
		$\psi(E_{des})$	distribution function of desorbed species

next two decades. This is true for China and India, as well.

About 91 kg of CO₂ are produced for every 100 kWh of electricity produced when a bituminous coal is burned in a pulverized coal-fired power plant having a first-law efficiency of 34%, an average value for present-day conventional plants. In light of the potential impact of CO₂ emissions on climate change, it is prudent to determine more efficient schemes for converting the energy in coal to electricity, schemes that minimize CO₂ emissions per kWh of electricity produced. The key to evaluating different power plant design strategies in a timely, cost-effective manner is the ability to predict accurately the performance of coal-based energy conversion processes. The key to obtaining accurate predictions is the development of accurate models of the processes that govern coal conversion to gaseous species. To this end, we have undertaken a study aimed at enhancing our understanding of char oxidation to carbon oxides.

A critical aspect of the overall char oxidation process is the heterogeneous chemical interactions occurring at the char surface. These interactions are functions of the physical surface of the char and the heterogeneous reactions that occur. While surface species are often viewed and modeled as having singular and specific kinetic properties, studies have provided strong evidence suggesting that surface complexes have no single nature. Instead they are characterized by a distribution of chemical properties due to the local microscopic irregularities typical of char surfaces.

During oxidation, besides the microscopic surface interactions that occur, yielding species distributions, macroscopic surface area changes due to evolution of the pore structure of the char also occur and impact the char conversion rate. During the course of char conversion, the total surface area of very microscopic chars must first increase as internal pore volume increases. Pore walls will then merge and coalesce, resulting in a decrease in surface area, eventu-

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