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Kinetic modeling of the oxidation of CO on Fe_2O_3 catalyst in excess of O_2

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ABSTRACT

This work addresses the oxidation of CO under oxygen-rich conditions using a Fe_2O_3 model catalyst. Based on in situ DRIFTS studies, isotopic labeling, and kinetic examinations performed in a gradient-free loop reactor an Eley–Rideal type mechanism is postulated. This mechanism includes the dissociative adsorption of O_2 on active Fe sites, followed by reaction of surface oxygen with gaseous CO, producing CO_2. Furthermore, a mean field model is constructed for numeric modeling and simulation of the CO oxidation, as well as calculation of the Fe_2O_3 surface coverage. The kinetic model represents a network of six elementary reactions using Arrhenius-based rate expressions. The comparison between measured and calculated data shows that the model describes the experiments well. Kinetic parameters for the elementary reactions are obtained from the literature or by fitting calculations. To reduce the number of free parameters, the patterns of O_2 TPD and CO_2 TPD are modeled numerically. To validate the model, the kinetic parameters are used to simulate catalytic data, which agree fairly well with the corresponding experimental results. The reaction of surface oxygen species with gas-phase CO is considered to be the rate-determining step in CO oxidation on an Fe_2O_3 catalyst. In addition, the thermodynamic consistency of the kinetic parameters is proven.

1. Introduction

Diesel engines exhibit the highest efficiency for automotive applications. As a consequence, their low fuel consumption leads to a reduced production of the greenhouse gas CO_2. However, a serious constraint of diesel engines is the emission of air pollutants, including hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_x), and soot [1]. Several after-treatment techniques for removing these pollutants from the oxygen-rich diesel exhaust have been developed [2,3]. The use of diesel particulate filters (DPFs) to decrease soot emissions has been studied. In such systems, the soot is mechanically separated from the exhaust stream. The accumulation of the soot necessitates a regeneration process, however. This regeneration can be performed discontinuously by increasing temperature through the postinjection of fuel combined with oxidation of the resulting unburned hydrocarbons and CO on a Pt precatalyst [4]. In addition, the ignition temperature of the soot can be lowered by the introduction of a cerium- or iron-containing fuel additive [4] or by a catalyst coated onto the DPF substrate, such as Pt or CeO_2 [5]. The continuous regeneration of DPF systems is provided by the continuously regenerating trap (CRT) technique, in which soot conversion is initiated by the strong oxidant NO_2 [6,7]. The required NO_2 is produced by oxidation of NO on a Pt precatalyst.

The use of selective catalytic reduction (SCR) and NO_x storage reduction (NSR) catalysts for the removal of NO_x from diesel exhaust has been studied. The NSR procedure is based on the periodic adsorption and reduction of NO_x [8–10]; the catalysts consist of precious metals, primarily Pt, as well as basic adsorbents, such as Al_2O_3 and $BaCO_3$. The platinum component supports the oxidation of NO into NO_2, which is subsequently stored by the adsorbents. When the storage capacity is reached, rich exhaust conditions are established momentarily by engine management systems, in which NO_x desorbs from the substrate and is reduced by H_2, CO, and hydrocarbons on the precious metals. A disadvantage of the NSR technique is the susceptibility of the basic adsorbents to sulfur poisoning [11]. In the SCR technique, NO_x is continuously reduced by NH_3 on TiO_2-supported WO_3/V_2O_5 catalysts, resulting in the selective formation of nitrogen [12,13]. The ammonia required for SCR can be produced on board by hydrolysis of nonhazardous urea, which is stored in another tank. But a disadvantage of the SCR procedure is the toxic nature of the V_2O_5 component; thus, harmless catalytic systems with promising SCR performance (e.g., the zeolite Fe-ZSM5) have been developed [14,15].

In contrast to soot and NO_x the pollutants HC and CO can be simply converted in the oxygen-rich diesel exhaust by using Pt or Pd oxidation catalysts [2]. The mechanism and kinetics of the catalytic oxidation of HC and CO on Pt have been investigated in depth by several groups [16–18]. Furthermore, numerous studies on nanosized Au catalysts useful for CO oxidation have been published [19], which demonstrate that these materials have in-

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sufficient thermal stability for practical applications. In addition, some iron-containing oxides also have been reported to be effective in CO oxidation, either as a catalyst (e.g., $LaFeO_3$ [20], $LaFe_{1-x}(Cu,Pd)_xO_3$ [21], $Fe_2O_3/Cr_2O_3/Al_2O_3$ [22], Fe_2O_3/SiO_2 [23]) or as a support (e.g., Au/Fe_2O_3 [24], Pd/Fe_3O_4 [25]). Little detail is available on the CO oxidation on Fe_2O_3 based catalysts, however. Consequently, the aim of the present work was to study the mechanism and kinetics of the oxidation of CO in an excess of O_2 using a α-Fe_2O_3 catalyst; α-Fe_2O_3 was used as the model sample to exclude interactions of the active sites with a specific support. Based on the mechanistic and kinetic examinations, a kinetic mean field model was constructed to provide insight into the reactions occurring on the surface of Fe_2O_3. The mechanistic examinations were carried out using both isotopic labeling and in situ diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS). The kinetic studies were performed with a gradient-free loop reactor, and temperature-programmed desorption of O_2 (O_2 TPD) and CO_2 (CO_2 TPD) was conducted to obtain independent kinetic parameters. Finally, for model validation, some simulations were carried out and thermodynamic consistency was proven as well.

2. Experimental

2.1. Catalyst preparation and characterisation

The Fe_2O_3 catalyst was synthesized by the polyvinyl alcohol method as described previously [26], with final calcination in air at 600 °C for 5 h. The catalyst was characterized by powder X-ray diffraction (PXRD), N_2 physisorption, and temperature-programmed reduction by H_2 (HTPR). The PXRD analysis was performed at room temperature on a Siemens D 501 with a Ni-filtered CuK_α radiation source and a rotating sample holder. N_2 physisorption was conducted with a Porotec Sorptomatic 1990. The sample was pretreated at 350 °C for 2 h in vacuum (10^{-4} mbar) and cooled to −196 °C, after which the N_2 isotherm was recorded. The BET surface area (S_{BET}) was derived from the adsorption data recorded at p/p_0 ratios of 0.05–0.30.

In HTPR, 29 mg of catalyst powder (according to 20 mg of Fe) was charged into the quartz glass tube reactor (6 mm i.d.) and fixed with quartz wool. Then the reaction mixture (5 vol% H_2, 95 vol% N_2) was added at a flow of 100 ml/min (STP), and the temperature was increased linearly to 900 °C at a rate of 20 K/min. The temperature was monitored by a K-type thermocouple located directly in front of the sample. The concentration of H_2 was measured continuously with a Shimadzu thermoconductivity detector. For the specific detection of H_2, the water formed was removed by passing the reactor effluents through a cold trap (−50 °C).

2.2. TPD studies

For CO_2 TPD and O_2 TPD, the catalyst was in granular form, to avoid discharge. The sample was pressed into pellets at a pressure of 40 MPa, granulated, and sieved to a size of 125–250 µm. Before TPD, the catalyst was pretreated in an N_2 flow at 500 °C for 30 min, to eliminate possible impurities and obtain reproducible conditions. Then it was cooled to 200 °C, at which point CO_2 or O_2 exposure was initiated. After saturation, the catalyst was flushed with N_2, and the temperature was increased linearly at a rate (β) of 10 K/min. In TPD studies, the total gas flow was maintained at 500 ml/min (STP) while the temperature was monitored by a K-type thermocouple installed directly in front of the sample.

CO_2 TPD was performed with 1.60 g of Fe_2O_3 in a quartz glass tube (11 mm i.d.), whereas exposure to CO_2 was done using a gas mixture of 2 vol% CO_2 and 98 vol% N_2 (Air Liquide). CO_2 was monitored by nondispersive infrared spectroscopy (NDIR) using a Fischer–Rosemount BINOS 5 spectroscope.

O_2 TPD was carried out with a catalyst mass of 15 g in a quartz glass tube (22 mm i.d.). In O_2 exposure, a blend of 2 vol% O_2 and 98 vol% N_2 (Air Liquide) was obtained. O_2 was analysed by chemical ionisation mass spectrometry (CIMS) using a V&F Airsense 500 spectrometer.

2.3. Kinetic studies

For kinetic studies, a commercial cordierite honeycomb (400 cpsi, $d = 10$ mm, $l = 30$ mm) was coated with the Fe_2O_3 catalyst. The substrate was dipped into a slurry of 1 g of grinded Fe_2O_3 ($d < 32$ µm) and 20 ml of water, then heated to 450 °C for 3 h in air. This procedure was repeated several times until a loading of 220 g/l was obtained, corresponding to 500 mg Fe_2O_3.

The kinetic studies were performed using a gradient-free loop reactor with an external gas cycle. The Fe_2O_3-coated honeycomb is packed into an 11-mm-i.d. quartz glass tube, fixed with quartz wool, and pretreated at 500 °C in O_2 flow for 15 min and then for another 15 min in N_2. Then the temperature in the N_2 flow was decreased to 230 °C, at which point the feed was added. The reaction mixture was a blend of the pure components (Air Liquide) dosed from independent flow controllers (MKS Instruments). The feed consisted of 400–7000 ppm CO, 6.0–99.3 vol% O_2, and balance N_2. The total volume flow was 400 ml/min (STP), with a recycling ratio, ψ ($\psi = F_{loop}/F_{out}$), of 110. The temperature was monitored by two K-type thermocouples located directly in front of and behind the honeycomb; the maximum difference of the inlet and outlet temperatures was found to be 10 K. CO and CO_2 were monitored by NDIR (Binos 1.2 for CO and Binos 4b.1 for CO_2, Leybold-Heraeus), and O_2 was detected with a magnetomechanic analyser (Magnos 6G, Hartmann & Braun). The reactor effluents were recorded after steady state was achieved.

In addition, for model validation, CO_2 also was dosed, in varying amounts. These experiments were conducted in an 11-mm-i.d. quartz glass tube reactor, which represented a plug–flow reactor. The total flow was 500 ml/min (STP), and the feed consisted of 7000 ppm CO, 20 vol% O_2, 0–79.3 vol% CO_2, and balance N_2 (Air Liquide).

Mass transfer limitations, which possibly could result from film and pore diffusion, were excluded by estimating the Mears and Weisz criteria [27].

2.4. Isotopic labeling

The isotopic studies were performed with $^{18}O_2$-labeled oxygen (Linde). The quartz glass tube reactor (11 mm i.d.) was charged with Fe_2O_3 granules (320 mg), after which the same pretreatment as described for the kinetic experiments was carried out. After cooling to 260 °C in N_2 flow, the feed, containing 470 ppm $C^{16}O$, 3000 ppm $^{18}O_2$ (Linde), and balance N_2, was added (500 ml/min; STP). The effluent was measured by CIMS.

2.5. DRIFTS studies

The surface species formed in the CO oxidation on Fe_2O_3 catalyst were studied by DRIFTS, using a Nicolet 5700 FTIR spectrometer (Thermo Electron) equipped with an MCT detector and DRIFTS optics (Thermo Mattson). The stainless steel IR cell had a KBr window and was connected to a gas-handling system. The spectra were recorded at 1000–4000 cm^{-1} with an instrument resolution of 2 cm^{-1}. A total of 250 scans per spectrum were accumulated, for a time resolution of 3 min. The temperature of the sample was monitored by a K-type thermocouple placed 2 mm underneath the crucible surface. During the measurements, both the spectrometer and the DRIFTS optics were purged with nitrogen, to avoid air diffusion into the system. Over 24 h, the spectrum of the fresh sample