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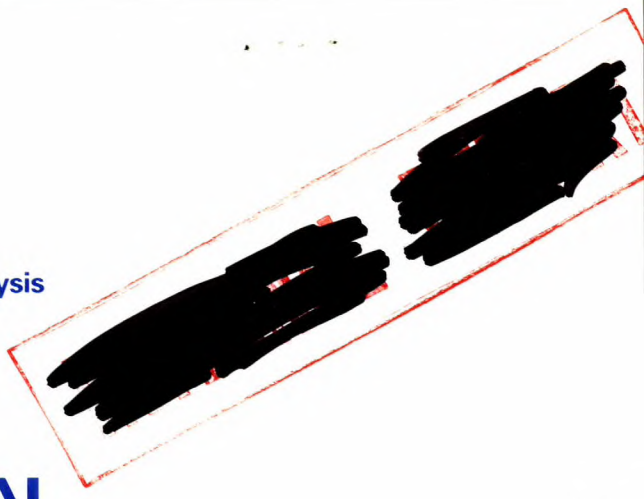

PROGRESS IN CATALYSIS

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OXIDATIVE REGENERATION OF HYDROTREATING CATALYSTS USING A LASER REACTOR

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ABSTRACT

An experimental reactor system is described for regenerating deactivated hydrotreating catalysts through oxidative coke burn-off using laser radiation. The laser reactor was designed to process batches of catalyst extrudates using a rotating bed principle involving sequential particle irradiation and agitation steps. The catalyst regeneration system contained dual CO_2 laser and agitation units to enhance processing efficiency. The experimental reactor was used to carry out a systematic study involving laser regeneration of spent commercial catalyst samples from an industrial hydrotreating unit. Carbonaceous deposits on the catalyst surface were removed by the photo-thermally induced chemical reaction of coke molecules with an oxidizing gas mixture. The unique properties of laser heating should reduce the deleterious effects of conventional coke burn-off such as sintering and metals agglomeration. A parametric study of the regeneration process was undertaken using an established experimental design procedure. Important processing parameters were found to be laser intensity, residence time, oxygen concentration, and gas flow rate.

INTRODUCTION

Conventional regeneration of hydrotreating catalysts involves coke burn-off in a high temperature furnace in the presence of a stream of oxidizing gas. This procedure results in the removal of coke which blocks active sites and plugs pores on the surface of catalyst particles. Such coke deposits are very complex and may consist of many kinds of carbonaceous species [1]. A variety of sulphur compounds may also be present.

Most sulphur appears to be removed at low regeneration temperatures and competes with carbonaceous material for oxygen during burn-off.

There are two fundamentally different modes in which oxidative regeneration may occur. At low reaction temperatures, kinetic factors involving collisions of oxygen molecules with coke are rate limiting. The rate of burn-off is sufficiently slow to allow adequate diffusion of oxygen to coke in the particle interior. At higher temperatures, mass transfer effects dominate [2]. The relative importance of these effects depends on such factors as the geometry of individual catalyst particles and particle packing density. They may also be influenced by the composition of the atmosphere in which regeneration occurs.

In conventional catalyst regeneration processes involving high temperature burn-off, the initial contact between the coke on the catalyst surface and the oxidizing medium may result in uncontrollable overheating with the possibility of sintering. However, temperatures as high as 500°C may be required for the efficient burn-off of carbonaceous material [3]. Such intense heating, while removing refractory coke molecules, may result in metals agglomeration and hence failure to restore the catalyst to its original level of activity.

In this paper we discuss an alternative method of regeneration of hydrotreating catalysts involving the use of infrared laser radiation to heat directly the surface of coked catalyst particles in a controllable manner such that the removal of carbonaceous material is achieved without the application of high temperatures for extended periods of time. We have demonstrated that sulphided Ni-Mo/γ-Al_2O_3 and Co-Mo/γ-Al_2O_3 catalysts may be effectively regenerated using this new technique.

EXPERIMENTAL

Since laser heating of materials occurs via surface interactions [4], the primary requirement of a laser-based catalyst regeneration system is a means to ensure that catalyst particles are evenly exposed to laser radiation [5]. Figure 1 shows the experimental configuration adopted.

For the experiments described, two CO_2 lasers operating in the slow axial flow configuration [6] provided two output beams each with power up to 80 W. Laser radiation was transmitted to the reactor in enclosed optical delivery systems by means of which the beams were focused so as to produce a broad beam at the surface of the catalyst bed. Each laser could be pulsed independently and the power in each beam could be programmed from a control system.

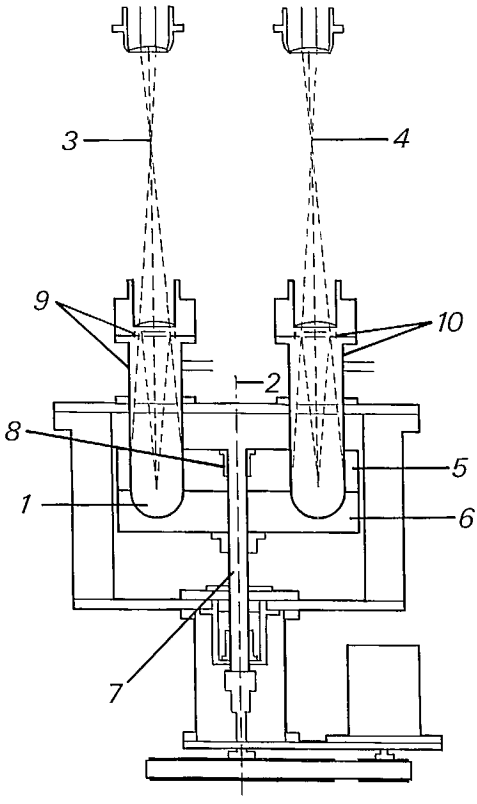

Figure 1. Cross sectional schematic of the laser catalyst regeneration reactor.

Catalyst particles were placed in an annular bed (*1*) which rotated about its axis *(2)*. The bed was fully contained in the interior of the reactor. The rotation of the bed moved the catalyst particles under the laser beams *(3,4)* then into an agitation region where a tangential gas flow from inlet nozzles caused random mixing of the particles. The reactor core consisted of an upper *(5)* and lower half *(6)*. The latter was rotated relative to *(5)* via the shaft *(7)* on the motor-bearing axis *(8)*. The windows and mounts *(9,10)* served to introduce laser radiation into the reactor while maintaining a tight seal.

Gases evolving from the catalyst bed under regeneration were removed through outlet ports. Gas for oxidative regeneration was introduced through a set of two nozzles mounted at 90° with respect to the optical parts.

An experimental design was set up to investigate the reactor operation and was optimized using Taguchi methods [7]. The independent variables chosen were A) laser intensity, B) dwell time, C) oxygen concentration and D) catalyst particle packing density. The dwell time (s) is defined as the amount of time a single catalyst particle is exposed to the laser beam with each pass. During laser regeneration the temperature of the catalyst bed was measured with a thermocouple located 1 cm downstream from the irradiation site. This thermocouple measured temperature just below the upper surface of the catalyst bed. Temperature was used as a critical response and not as a factor in the experimental array since it is determined by factors A-C above. Using these variables an L_9 Taguchi array was constructed. Since it was observed that laser intensities, I, in excess of 100 W cm^{-2} led to fracturing of catalyst particles, this was the maximum intensity used for regeneration. In this study the total gas flow rate was maintained at 15 L min^{-1} (air) while the total photo-thermal energy per unit mass of catalyst was kept constant at 17.3 kJ g^{-1}. Table 1 summarizes the range of process variables used in the Taguchi matrix.

Table 1.
Range of variables used in laser regeneration runs

Variable		Value		
		Low	Medium	High
Laser intensity	(W cm^{-2})	35	50	100
O_2 concentration	(%)	20	60	80
Dwell time	(sec)	0.4	0.8	1.6
Packing density	(batch size g)	10	25	50

Samples of coked commercial Ni-Mo/γ-Al_2O_3 hydrotreating catalyst (Criterion 424, 1/16 in. extrudates) were obtained from Syncrude Canada Ltd. Samples were analyzed using scanning electron microscopy (SEM) techniques using an Hitachi S520 instrument with a beam energy of 25 kV. Elemental analyses on regenerated and coked samples were carried out using proton induced X-ray emission spectroscopy (PIXE). Surface functional groups were assessed before and after regeneration by Fourier Transform Infrared spectroscopy using a Nicolet 205X instrument in the diffuse reflectance mode at a spectral resolution of 0.5 cm. Whole catalyst extrudates were analyzed after purging the

system with inert gas.

For comparison, samples of the same coked commercial hydrotreating catalyst were regenerated in a conventional furnace and were subsequently analyzed along with laser regenerated samples.

RESULTS AND DISCUSSION

Typical temperature vs. time plots for two different laser regeneration runs are shown in Figures 2 and 3 respectively. The catalyst bed temperature recorded is the downstream

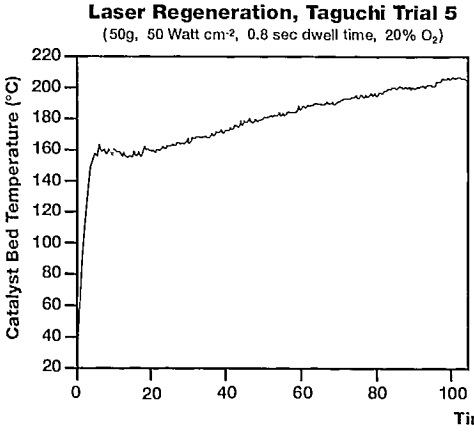

Figure 2. Catalyst bed temp. profile. Medium dwell time, low O_2 concentration.

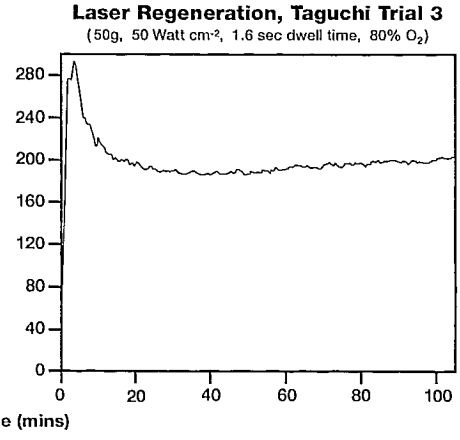

Figure 3. Catalyst bed temp. profile. High dwell time, high O_2 concentration.

temperature after laser irradiation. In Figure 2 (low O_2 concentration, medium laser intensity, medium dwell time) a gradual temperature rise is observed over the entire irradiation period. This treatment gave little regeneration of the catalyst particles. Figure 3 (high O_2 concentration, medium laser intensity, high dwell time) shows the temperature profile obtained in another batch in which regeneration as estimated from surface inspection and from PIXE measurements of sulphur concentration was close to 100%. The initial temperature spike is thought to arise from burn-off of lightly held reactive coke molecules as well as some sulphides. This peak is enhanced by the high O_2 concentration and longer dwell time.

Table 2 presents examples of catalyst regeneration runs

using both conventional and laser processing methods. In the latter case the effects of changing operating parameters may be observed in terms of percent regeneration and PIXE elemental analysis of regenerated materials. Percentage regeneration was determined based on sulphur removal. The bulk concentrations of Mo and Ni in fully regenerated catalysts are consistent with those found in the commercial product prior to presulphiding. Significant amounts of Fe were detected in both coked and regenerated samples. The Fe contaminant was found concentrated in the outer 30% of the catalyst extrudate as shown by SEM analysis.

Table 2.
Examples of catalyst regeneration runs using both conventional and laser processing

	Regeneration Conditions				% Regen.	Elements Wt % (PIXE)			
Samp. No.	Mass (g)	I (W cm^{-2})	Dwell (sec)	$[O_2]$ (%)	from [S]	[S]	[Fe]	[Mo]	[Ni]
1		Conv. Regen.			83	2.06	0.66	12.19	3.18
2		Conv. Regen.			100	0.90	0.18	11.07	2.66
3	50	50	1.6	80	100	0.68	0.36	12.13	3.31
4	50	35	2.4	80	99	0.97	0.25	10.74	2.62
5	50	100	1.0	60	100	0.56	0.15	11.03	3.28
6	25	50	0.4	80	49	4.44	0.17	10.12	2.49

A summary of average elemental concentrations for conventional and laser regenerated samples is given in Table 3. It is apparent that the amounts of Mo and Ni in samples processed via the laser reactor are similar to those obtained after conventional thermal regeneration. The level of regeneration as estimated from the sulphur concentration is also similar in both processes. The extent of regeneration as judged by visual inspection was usually 100% in conventional runs with exposures of 1 h at 500°C.

Table 3.
Comparison of elemental analyses obtained from PIXE data (average values) for furnace and laser regenerated Ni-Mo catalyst.

Method	% Regeneration from [S]	Elemental Composition Wt % [P]	[Fe]	[Mo]	[Ni]
Furnace	93	2.72	0.42	11.13	2.81
Laser	92	2.80	0.25	11.00	2.83

The FTIR spectrum of a sample of coked Criterion 424 Ni-Mo/γ-Al_2O_3 catalyst (Figure 4) exhibits strong absorption over a broad spectral range indicating the presence of carbonaceous materials [8]. Peaks at 2940 and 1450 cm^{-1} are indicative of C-H vibrations of surface functional groups. A corresponding spectrum for laser regenerated Ni-Mo catalyst is shown in Figure 5. Evidence for CH_n groups has disappeared and also the broad background absorption in the 4000 - 2000 cm^{-1} region indicating removal of carbonaceous material. Surface hydroxyls are present on the laser regenerated material as evidenced by the broad absorption near 3500 cm^{-1} and the peak at 1630 cm^{-1}. Features in the 1250 - 900 cm^{-1} range are similar to those observed in unused catalyst and can be associated with MoO_3 and Al_2O_3 vibrations.

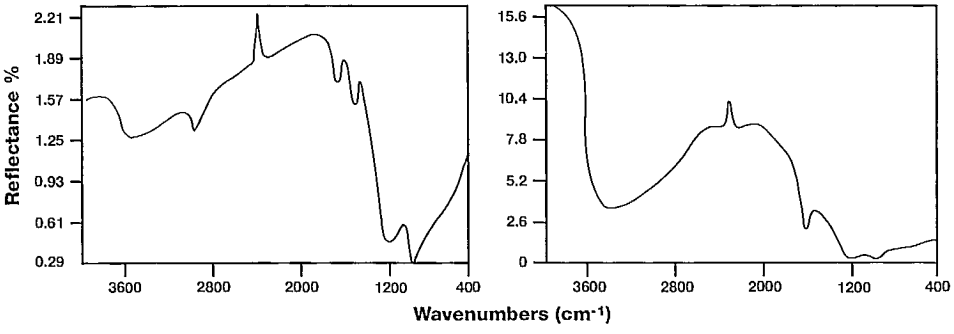

Figure 4. FTIR spectrum of coked Ni-Mo hydrotreating catalyst.

Figure 5. FTIR spectrum of laser regenerated Ni-Mo catalyst: I=35 Watt cm^{-2}, 80% O_2, dwell time 2.4 s.

The observation of a distinct boundary between regenerated and unregenerated regions in partially laser treated coked particles suggests that laser regeneration occurs under strong

limited mass transfer conditions [2]. As a result, all of the O_2 that comes into contact with coked material will be consumed. The rate of burn-off will be completely controlled by the rate of diffusion of O_2 into the catalyst pores and the rate of removal of gaseous products. Since mass transfer effects appear to dominate, there is a good possibility that mathematical modelling of the laser regeneration process may be feasible. This contrasts with the lack of a simple model for conventional regeneration of hydrotreating catalysts such as is available for FCC regeneration [9].

CONCLUSIONS

A new catalyst regeneration technique based on heating with CO_2 laser radiation in a novel reactor has been described. This process offers an alternative method of regenerating hydrotreating catalysts allowing close control over heating conditions. The chemical composition and structural integrity of catalysts regenerated in this way are comparable to that obtained using a conventional furnace. It was found that 100% laser regeneration of fully coked catalyst required individual particle integrated exposure times of about 60 s. in an atmosphere enriched in oxygen (20-80%) using a laser intensity of 50 W cm^{-2}. Regeneration appears to occur under strong limited mass transfer conditions. Full details of the Taguchi analysis of experimental data will be presented in a future publication.

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