

[262g] - Microfibrous & Micro-Structured Adsorbents and Catalysts Media: Enhancement in Effectiveness Caused by Static Mixing

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Microfibrous entrapped catalysts and sorbents are a new class of material that consists of micron sized catalyst/sorbent particles (e.g. 25–250 microns) entrapped in a mesh composed of micron diameter fibers (2–20 microns)¹⁻⁵. These fibers can be made out of metals, ceramics or polymers⁶. Microfibrous materials have inherent advantages such as high contacting efficiency, low intra-particle transport resistance, improved heat & mass transfer, and low pressure drop. These materials are engineered to provide specific void volumes and cage dimensions by adjusting the fiber loading and fiber diameter. The resultant cage is used to entrap sorbent/catalyst particulates. The overall void volume of the final structure varies from ca. 50-98%. Enhanced heat and mass transfer is caused by micro scale mixing produced by the fibers. The micro scale mixing also results in plug flow characteristics inside the microfibrous meshes. The drag on the micro fibers in the mesh focus the flow between the fibers resulting in higher interstitial velocities impacting the entrapped particulates resulting in increased mass transfer rates.

Low temperature CO oxidation, Preferential CO oxidation and VOC adsorption have been studied as model reactions to determine the nature of anomalous reactivity enhancements observed using microfibrous materials. Our results indicate that reactivity in microfibrous beds entrapping 150-250 micron diameter catalyst/sorbent particles is significantly higher compared to packed beds of the same particle size at equivalent catalyst loadings and face velocities. This effect has been attributed to static mixing imparted by the micro-fibers. This paper discusses a number of different effects observed in microfibrous media compared to packed beds, including: (i) fiber diameter versus contacting efficiency, (ii) reduction of boundary layer limitations, (iii) increase in volumetric reaction rate, and (iv) overall enhancement in heat and mass transfer.

Experimental

Four different tests were done for both low temperature CO oxidation and preferential CO oxidation. These four cases demonstrate the effectiveness of microfibrous media in enhancing reactivity of particulate catalysts. The baseline for comparison is a packed bed of the particulate catalyst. The second is a microfibrous mesh entrapping particulates of the same size. The third case is a packed bed diluted with inert catalyst support to the same volumetric catalyst loading as the microfibrous mesh. The final test is a packed bed layered with microfibrous mesh.

Experimental conditions for the demonstrations were all done at temperature of 25°C at atmospheric pressure and particle size of 150-250 μm . The microfibrous media for both of the CO oxidation tests used nickel fibers of 4 and 8 μm in a weight ratio of 1:3. The nickel fibers, particulates and cellulose are cast into a preform by wetlay papermaking technique. The resulting preform is sintered at 950°C in H_2 atmosphere for 30 minutes. The sintered media contains approximately 18 vol. % particulates, 1.6 vol. % fibers and ca. 80 % bed voidage. Both of the CO oxidations of sintered media were done in an 8 mm I.D. tube with bed depth of 1 cm. The packed beds of catalyst powder were tested in a 4 mm ID tube. Each test

employed the same amount of catalyst powder. Other conditions for low temperature oxidation of CO were as follows: Transition metal promoted platinum on silica gel catalyst ($\text{Pt-M}_A\text{-SiO}_2$), inlet CO concentration of 2500 ppm, GC detection limit is 40 ppm CO, oxygen concentration of 20% with balance nitrogen, face velocity of 8 cm/sec, relative humidity of 86%. The CO oxidation catalyst deactivates due to reactant inhibition, so conversion as a function of time data is shown as Figure 1.

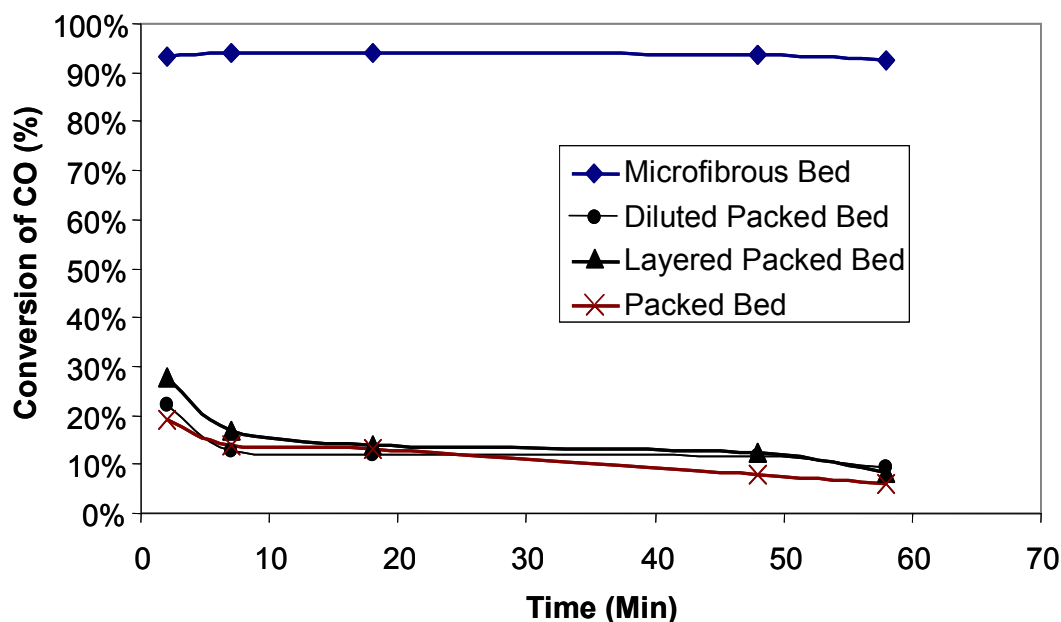


Figure 1. Low Temperature Oxidation of CO by $\text{Pt-M}_A\text{/SiO}_2$ Catalyst.

Other experimental conditions for preferential oxidation of CO from practical reformates were as follows: GHSV calculated based on the volume of catalyst, the catalyst is a transition metal promoted platinum on alumina, $\text{Pt-M}_B\text{/Al}_2\text{O}_3$, flowrate ratio $\text{CO/O}_2 = 1/1$, composition of practical reformate used is: 1% CO, 20% CO_2 , 40% H_2 , and balance N_2 . An additional set of measurements were taken using 1.5-2.5 mm catalyst pellets. The face velocity in these experiments was varied from 1-12 cm/s. Conversion of CO versus GHSV data for preferential oxidation of CO from practical reformates is shown as Figure 2.

VOC adsorption tests were done using n-hexane. These tests were done with in a 25 mm ID tube with down flow of the challenge vapors through the packed beds at a face velocity of 6.6 cm/s. Packed beds of the ACP powder, sintered powder and diluted powered were made. Five different samples of microfibrous media were prepared for testing. The five samples were prepared with mixtures of different diameters of nickel fibers to test the effect of fiber diameter. One square foot performs were prepared using an M/K sheet former with a recipe of 3 gm of cellulose, 12 gm of nickel fibers and 25 gm of 150-250 μm PICA activated carbon powder (ACP). The nickel fibers used in the recipes for the five performs were: (i) 8 μm , (ii) 3:1 ratio of 8&4 μm , (iii) 4 μm , (iv) 3:1 ratio of 4&2 μm , and (v) 2 μm . These samples were sintered in a fifteen inch wide-forty foot continuous belt furnace from BTU, Inc. with the hot zone at 950°C in an H_2 atmosphere. The entrance and exit of the furnace were blanketed with N_2 curtains. Belt speed of 4 inches per minute was used resulting in a soak time of 30 minutes. A sample of the ACP was sintered in a lab furnace at similar conditions to test the effect of the sintering process on its adsorption properties. For the VOC breakthrough test with

hexane, eight pieces 1-½ inch diameter were cut out with a leather punch. The eight layers of microfibrus supported sorbent media (MSSM) were put into the joint of the 25 mm glass tube and the edges sealed with hot glue.

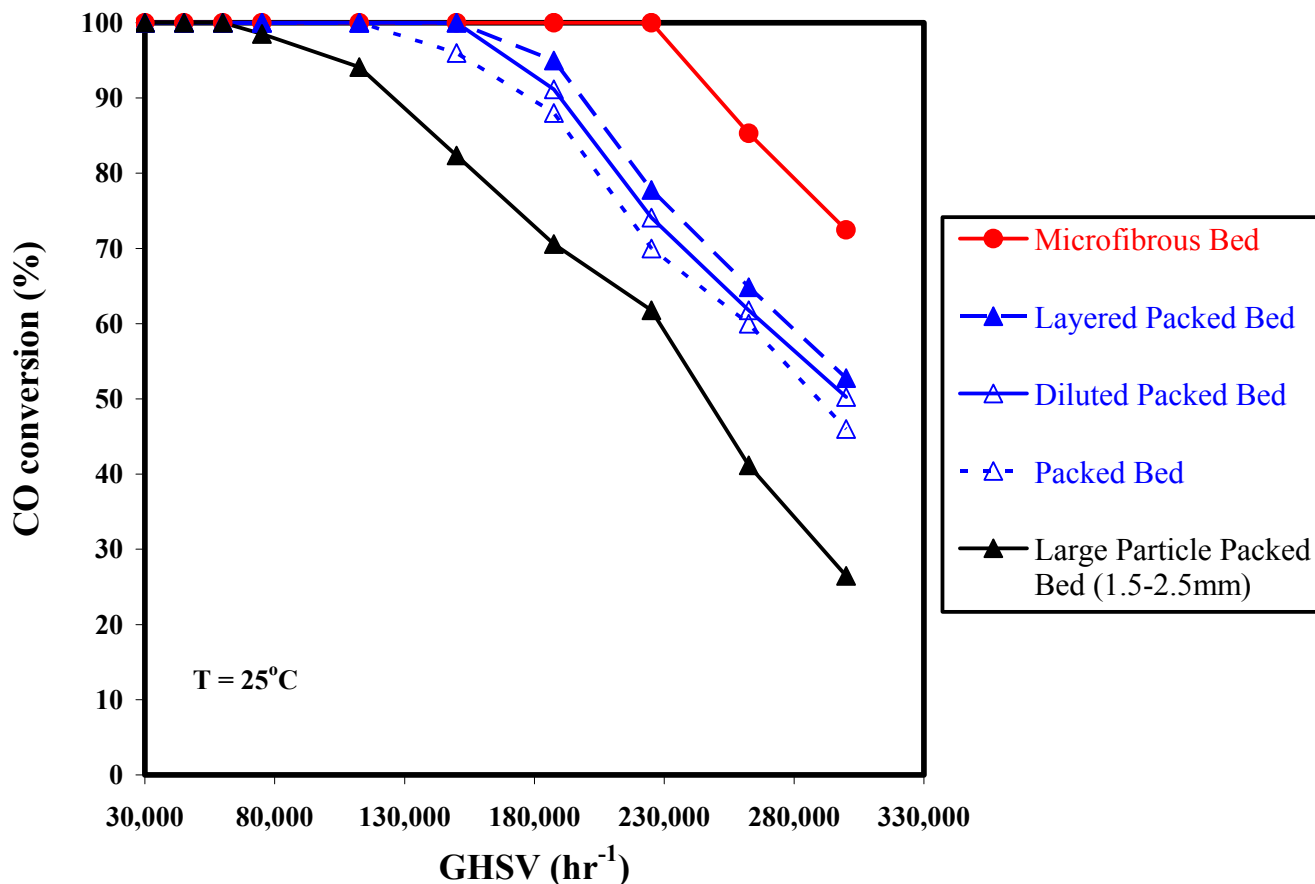


Figure 2. Low Temperature Preferential Oxidation of Practical Reformate for PEM Fuel Cell over Pt-M_B/Al₂O₃.

Dry house air (5 SCCM) was metered through a bubbler filled with n-hexane and diluted with makeup air (2 SLPM) to a concentration of ca. 310 ppm. The outlet concentration was sampled every 5 sec by MultiRAE PID detector from RAE, Inc. The detector was calibrated with 100 ppm isobutylene before each measurement. Approximately 1.45 gm of ACP was used in each measurement of MSSM or ACP. The samples of ACP were supported by a layer of Hollinee E200 filtration media and then covered by a layer of 5 gm of 150-212 μm glass beads to prevent channeling. The diluted ACP sample was prepared by mixing the ACP with 10 gm of the glass beads to reduce the volume loading of ACP in the bed to that in the MSSM. The diluted bed sample was also covered by a 5 gm layer of glass beads. VOC breakthrough curves normalized to 310 ppm challenge are shown as Figure 3.

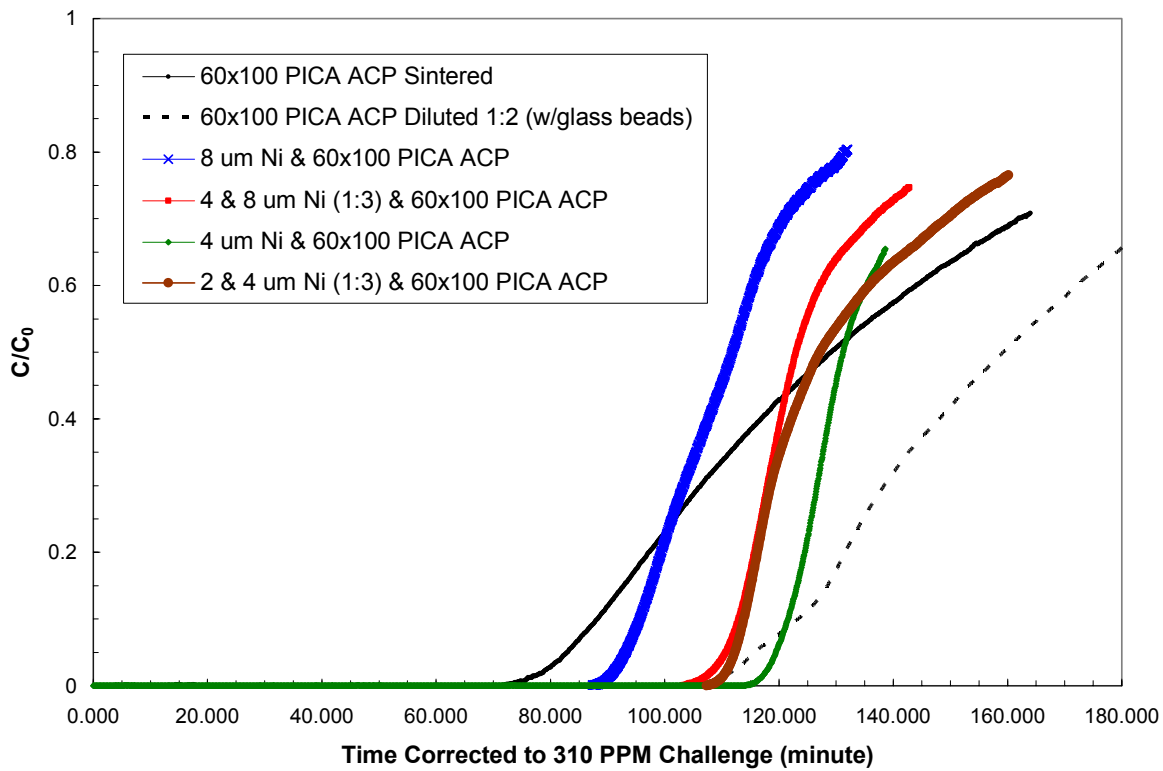


Figure 3. Hexane Breakthrough Curves for PICA ACP and Several MSSM.

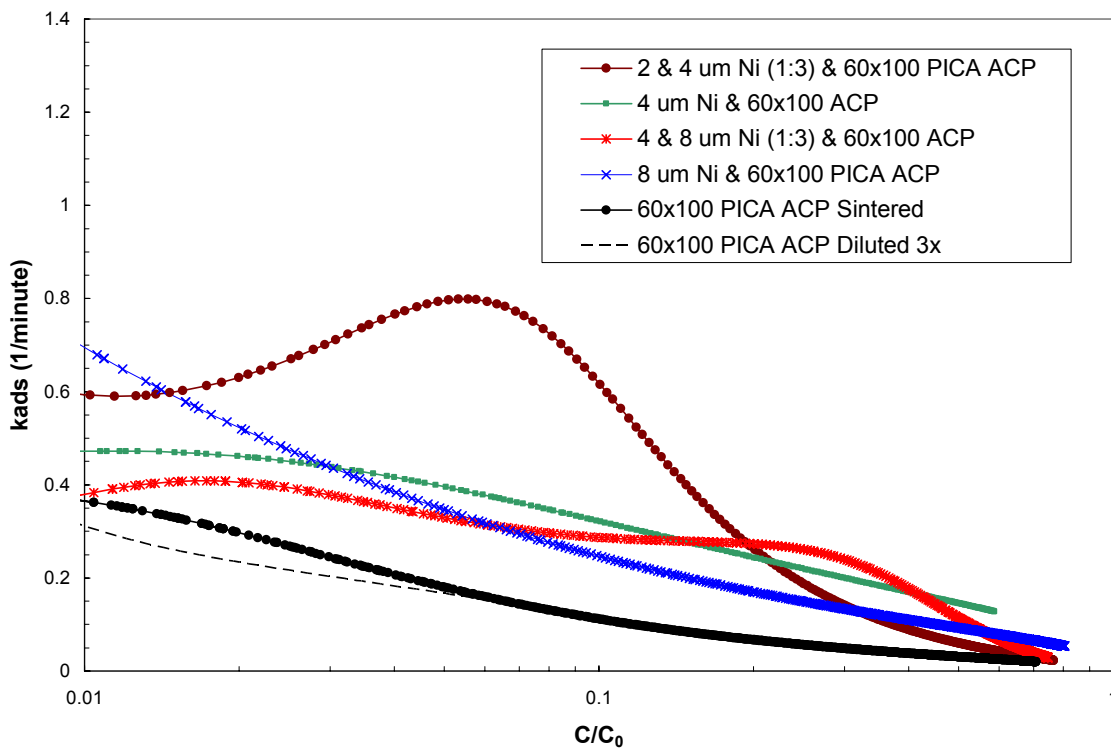


Figure 4. Instantaneous Adsorption Rate Constants from Hexane Breakthrough Curves.

Results and Discussion

Conversion of CO by Manganese promoted Platinum on silica at low temperature is shown in Figure 1. Conversion is plotted against time since the reaction is deactivated by reactant poisoning. The results for the three different packed beds of catalyst particles are all about the same. At ten minutes after the reaction was started the conversion for the three packed beds are about fifteen percent and for the microfibrinous mesh it is about ninety-five percent. If a rate constant is calculated from these data it indicates that the reaction rate for the catalyst in the microfibrinous mesh is about 1.8 times higher than for the packed beds. The microfibrinous mesh catalyst also shows less deactivation during the experiment than the packed beds.

Steady-state conversions for preferential oxidation of CO in the presence of H₂ shown in Figure 2 demonstrate that microfibrinous entrapped catalysts are more effective than beds of catalyst particles of the same size. The microfibrinous entrapped catalyst completely oxidized CO at GHSV up to 230,000 hr⁻¹. The layered packed bed and diluted packed beds had 100% conversion up to GHSV of 150,000 hr⁻¹ and the packed bed had 100% conversion up to GHSV of 100,000 hr⁻¹. A first order lumped rate constant would be the GHSV times natural logarithm of one minus the conversion. The results shown in Figure 2 indicate an approximately two fold higher rate constant for the catalyst entrapped in microfibrinous mesh versus packed beds of catalyst.

The VOC breakthrough curves shown in Figure 3 were analyzed in terms of the Bed Depth Service Time equation⁷. This equation is given as follows:

$$t = \tau - \frac{\ln\left(\frac{C_0}{C} - 1\right)}{k_{acs} C_0}, \quad k' = \frac{dt}{d\left[\ln\left(\frac{C_0}{C} - 1\right)\right]}^{-1} \quad [1a,b]$$

The breakthrough data was plotted in the form of time versus $\ln(C_0/C-1)$. An instantaneous adsorption rate constant can then be estimated by taking the derivative of trend lines fitted to the n-hexane breakthrough data. Instantaneous adsorption rate constant is plotted in Figure 4 versus dimensionless concentration. The results from the VOC adsorption measurements are similar to the low temperature CO oxidation studies shown in Figures 1 and 2. The instantaneous adsorption rate constants are about twice as high for ACP entrapped in microfibrinous mesh versus packed beds of the same particles. The trend is for adsorption rate constant to increase as the fiber diameter is reduced. This could be expected as a smaller diameter requires more length of fiber for the same volume loading of fibers, and results in increased micro mixing.

A comparison of packed beds, microfibrinous materials and monoliths⁸ in terms of reaction rate divided by pressure drop will also be presented. Use of these materials in polishing sorbent filters⁹ has been presented previously. The polishing filter approach combines the high volumetric loading of a packed bed with the high contacting efficiency of microfibrinous materials. This allows the entire sorption capacity of the packed bed to be utilized by the polishing sorbent filter.

More fundamental studies of the effect of microfibers on mass transfer rates are planned. CO oxidation by Pt/Al₂O₃ catalysts at elevated temperatures is mass transfer controlled and will serve as a probe reaction to investigate the effect of microfibrous mesh on mass transfer rates of entrapped catalysts. Residence time distribution and temperature dispersion studies may be used to investigate the favorable characteristics of these microfibrous materials. 2-D CFD studies are in progress to study the velocity distributions inside these meshes. 3-D CFD computations will be undertaken in the next year.

Conclusion

Microfibrous materials entrap particulate catalysts in a robust mechanically stable matrix which improves their reactivity by reducing heat and mass transfer limitations. These materials may be produced from metal, polymer or ceramic fibers. These materials can be sintered to support structures and packaged in any desired form.

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