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Transient Studies of Low Temperature Catalysts for Methane Conversion

directed by

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BRIEF SUMMARY OF PROGRESS

This report summarizes results related to a new approach using fast flow low residence time to the production of synthesis gas from methane. A series of transient experiments were conducted over Rh and Zr promoted TiO_2 catalysts to determine the effect of surface interactions of methane and oxygen and the catalysts surface.

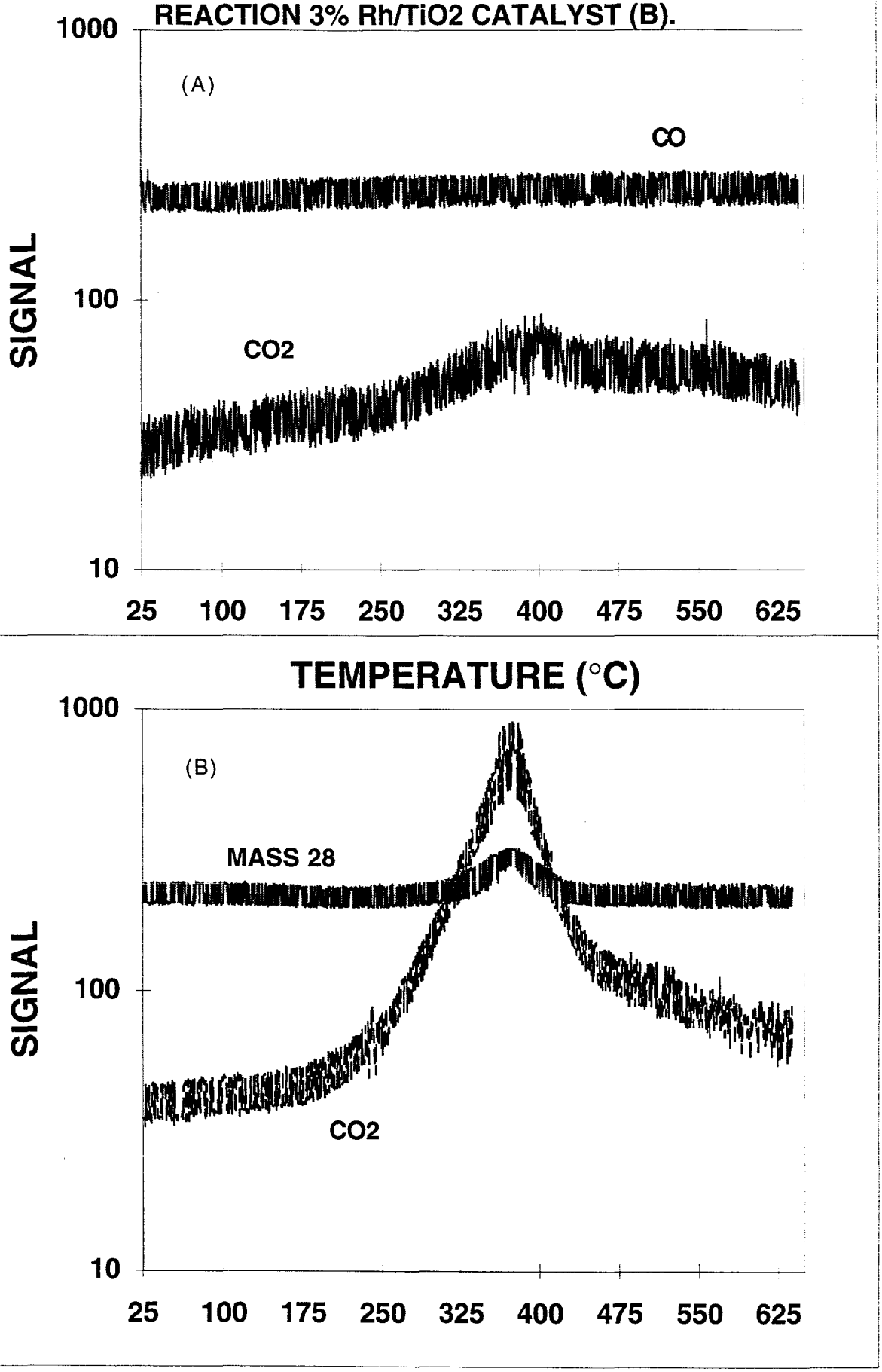
SUMMARY OF PROGRESS.

Previous results showed that a 3% Rh/TiO_2 catalyst was active during synthesis gas formation at temperatures significantly lower than those previously reported in the literature. In order to better understand the nature of the surface interactions between reacting gases and the catalyst surface, a series of transient experiments were conducted. The experiments consisted of pulses of methane and oxygen/methane mixtures diluted in helium carrier gas. In addition, temperature programmed desorption (TPD) studies were carried out on the fresh and used (post-run), Rh/TiO_2 catalyst. The purpose of this study was to learn about the effect of the long residence time reaction on the surface activity of the catalyst. The objective of the pulse experiments was to determine the role of surface and lattice oxygen during methane activation process. These experiments, combined with isotopic exchange experiments, could explain the activities and selectivities observed for the catalysts used in this study.

Fig. 1 a & b presents results of two different TPD experiments conducted on fresh and post-run (24 hrs. time on stream) 3% Rh/TiO_2 catalyst. During a TPD experiment, 10 mg of the catalyst were placed in the reactor. Helium was used as a carrier gas, flowing at 80 cc/min while the reactor temperature increased linearly. A UTI 100C mass spectrometer was used to analyze the reactor effluent. As it can be seen from the graph, the only product desorbing during this experiment is carbon dioxide. In both cases the amount of CO_2 is comparable, indicating that no significant readsorption of the CO_2 product takes place during synthesis gas formation. This result is consistent with previous observation of constant activity since adsorption of the reaction product is often related to the decrease of the catalyst activity. Previously , we found that the activity of Rh promoted catalyst remains constant over a period of twenty four hours for which time on stream experiment was conducted.

Fig. 2 presents results of methane pulse experiment over Rh promoted TiO_2 catalyst. During these experiments, pulses containing 4000 ppm of methane diluted in helium were sent into the reactor at 500 °C. The flow of the helium carrier was maintained at 80 cc/min. It is seen that during the methane pulse, the signal for the CO_2 product is the only one observed. Similar pulse experiments conducted on unpromoted TiO_2, did not show formation of any products. Also, it should be noted that the unpromoted catalyst, (TiO_2), is not active during synthesis gas formation and does not yield any products at 200-500 °C temperature range. The results of the pulse experiments suggest that the presence of the promoter , in this case Rh, is very important for the activity of the catalyst. In addition, the presence of the oxygen in the CO_2 product indicates that methane interacts with the surface of the catalyst and reduces it. The question which should be addressed also is: what is the origin of the CO which is not seen during pulse experiment, however, is a main reaction product during steady state experiments over the above catalyst. There are two possible explanations for this apparently different results. One, is that carbon monoxide is formed as a surface intermediate which is further oxidized to CO_2 at long residence times. In order to support this hypothesis additional pulse experiments at high flow rates of carrier gas should be conducted. The experimental apparatus will be modified in order to conduct transient studies at high gas flow rates. These experiments and results of isotopic studies which are underway will allow for definitive conclusions concerning the mechanism for the formation of CO at low residence time. These results will allow for the better understanding of the synthesis gas formation reaction on the Rh promoted titanium oxide catalyst.

FIG. 1. TPO EXPERIMENT OVER FRESH (A) AND POST REACTION 3% Rh/TiO2 CATALYST (B).



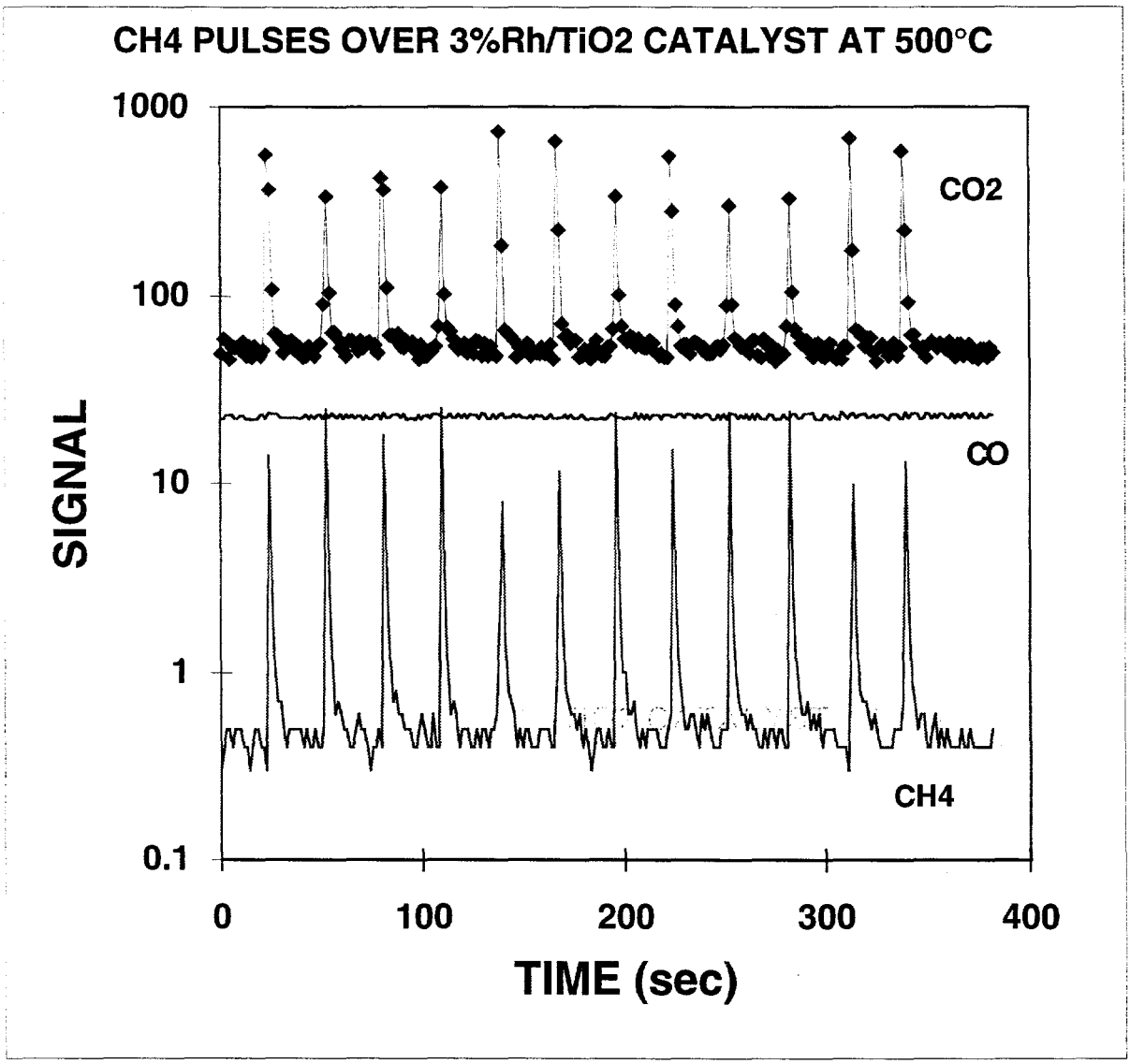


Fig.2 CO2 IS THE ONLY REACTION PRODUCT, NO CO WAS DETECTED
TPR WITH O2 DID NOT SHOW CONSUMPTION OF OXYGEN