JOURNAL OF CATALYSIS 69, 227–229 (1981)

Interactions of Methane with ThO_2/SiO_2 Surface at 1073 K

Methane decomposition over ThO_2/SiO_2 surface was investigated at 1073 K. Positive catalytic effect on the decomposition has been confirmed at low reaction conversions when ethane and ethylene are major products. Yields of ethylene and minor unsaturated hydrocarbons were sensitively inhibited by the presence of NO impurity in the methane feed.

Homogeneous decomposition of methane at a temperature of 1500°C is an industrial process for acetylene production (*1*). Major products of this homogeneous pyrolysis at low reaction conversions are ethane, ethylene, propylene, acetylene, and allene (*2*). The generation of each product has an induction period. These induction periods increase in the order $C_2H_6 > C_2H_4 > C_3H_6, C_2H_2 > C_3H_4$. This sequence indicates that products with a long induction period come from a further interaction of the accumulated preceding compound in the sequence. A radical reaction mechanism has recently been established for these observations (*2*).

Efforts on using catalysts such as iron, nickel, cobalt, copper, platinum, and palladium to increase the acetylene yield from methane pyrolysis were not successful. Only negative effects on acetylene yield were found for these metals (*3*). Whether the surface can catalyze the decomposition of methane at low reaction conversions, however, remains an unsolved question.

At room temperature methane molecules chemisorb slightly on surfaces (*4*). H_2 evolution accompanies this chemisorption at 500 K. Although carbide formation on the surface has been proposed, no unsaturated hydrocarbon product in the gas phase was detected from the methane–surface interaction around this temperature (*4, 5*). Since methane becomes unstable, relative to unsaturated compounds, under elevated temperatures (*6*), decomposition of methane over oxide surfaces was therefore studied at a temperature of 1073 K. ThO_2/SiO_2 was selected as the catalyst because it was shown to have good activity in a screen test (*7*).

A 13% ThO_2/SiO_2 catalyst was prepared by impregnating a calculated amount of thorium nitrate solution on silica gel. The impregnated catalyst was then dried and calcined at 1123 K for 16 h. The calcined catalyst has a specific surface area of 32 m^2/g, an apparent bulky density (ABD) of 0.91 g/ml, and a grain size of 30–60 mesh. A flow system equipped with a Matheson mass flow meter and gas-handling manifold was used. Purified Matheson methane (with only 0.2 ppm C_2H_6) at a controlled pressure of 15 Torr was decomposed in a 10-mm-i.d. quartz tubing containing 4.0 g calcined ThO_2/SiO_2 catalyst at 1073 K. Precaution was taken to exclude O_2 by pumping the system to less than 10^{-3} Torr. The catalyst was flushed with H_2 at the reaction temperature before each experiment. Trace amounts of adsorbed O_2, if any, were thought to be excluded by this treatment. Oxides such as ThO_2 and SiO_2 are not reduced appreciably at this temperature. Deposited coke was burned out by flushing the catalyst at 1073 K with O_2 before the hydrogen treatment.

Ethane, ethylene, acetylene, and propylene are also observed as the products of this methane–surface interaction. Figure 1 depicts the variation of the observed product distribution with contact time. The calculated rate of product generation is about 300 times faster than that of homogeneous decomposition in the gas phase. Also note in this figure that the induction period se-

0021-9517/81/050227-03$02.00/0
Copyright © 1981 by Academic Press, Inc.
All rights of reproduction in any form reserved.

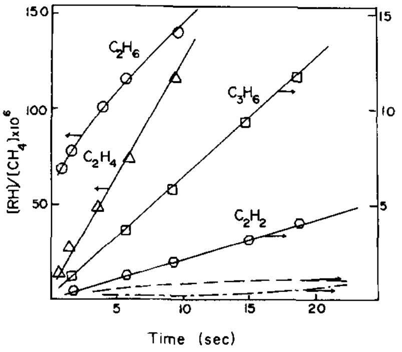

FIG. 1. The variation of product distribution with time when 15 Torr methane was decomposed over 13% ThO_2/SiO_2 at 1073 K. Data of homogeneous decomposition are also included for comparison with ethane (– – –) and ethylene (- - - -)

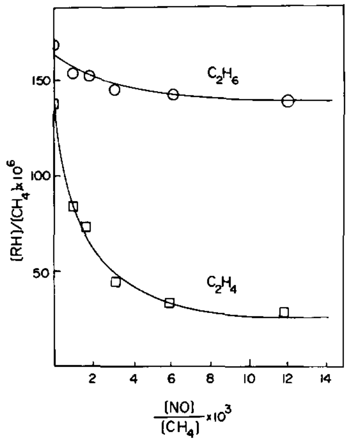

FIG. 2. The effect of NO on methane decomposition over ThO_2/SiO_2.

quence found in the homogeneous pyrolysis does not exist in this catalytic cracking. A surface interaction mechanism is therefore needed for these observations.

Two primary reactions can be conceived from the methane–metal oxide interaction, i.e.,

$$CH_4 \rightleftarrows CH_3(ads) + H(ads), \quad (1)$$

$$CH_4 \rightleftarrows CH_3 + H(ads). \quad (2)$$

Although reaction (2) has never been reported, this reaction should become favorable under the present unusual high temperature condition.

Ethane, the major product, may then be produced from the combination of methyl radicals, in the gas phase or absorbed on the surface, i.e.,

$$2CH_3 \rightarrow C_2H_6, \quad (3)$$

$$2CH_3(ads) \rightarrow C_2H_6. \quad (4)$$

Since the formation of unsaturated hydrocarbons does not have a noticeable induction period, these compounds must have been generated mainly by a route that does not require ethane as a metastable intermediate. The following surface reactions are therefore proposed,

$$CH_3(ads) \rightleftarrows C_nH_m(ads) + (3n - m)H(ads), \quad (5)$$

$$C_nH_m(ads) \rightleftarrows C_2H_4, C_3H_6, C_2H_2, \quad (6)$$

etc., where C_nH_m denotes surface intermediates (CH_2(ads), C_2H_5(ads), etc.)

Nitric oxide has been reported as a selective poison for surface hydrocarbon reactions (*8*). It would be of interest to investigate the effect of NO on methane decomposition. In the case of homogeneous pyrolysis at 1073 K, no substantial change was observed with the concentration of nitric oxide in methane up to 5000 ppm. A negligible scavenging effect of nitric oxide on the gas-phase intermediate (H, CH_3, C_2H_5, etc.) is therefore indicated. On the other hand, NO caused remarkable changes in the product distribution of catalytic cracking of methane. Yield of unsaturated products diminished drastically with NO concentration. Ethane, the only saturated product, decreased only slightly (see Fig. 2). A speculative explanation for these observations is that reaction (1) or reaction (5) mentioned above may be inhibited by the presence of NO.

ACKNOWLEDGMENT

We are grateful for the support of the National Science Council of the Replublic of China.

REFERENCES

1. Brownstein, A. M., "Trends in Petrochemical

Technology." Petroleum Pub., Tulsa, Okla., 1976.

2. Chen, C.-J., Back, M. H., and Back, R. A., *Canad. J. Chem.* **53,** 3580 (1975); **54,** 3175 (1976).
3. Wheeler, R. V., and Wood, W. L., *Fuel* **7,** 535 (1928); Stanley, H. M., and Nash, A. W., *J. Soc. Chem. Ind.* **48,** 1 (1929).
4. Frennet, A., *Catal. Rev. Sci. Eng.* **10,** 37 (1974).
5. Aika, K.-I., and Lunsford, J. H., *J. Phys. Chem.* **81,** 1393 (1973).
6. Duff, R. E., and Bauer, S. H., *J. Chem. Phys.* **36,** 1754 (1962).
7. Fang, T., M.S. dissertation, National Tsing-Hua University, 1978.
8. Millman, W. S., and Hall, W. K., *J. Phys. Chem.* **83,** 427 (1979).

TRELIANT FANG
CHUIN-TIH YEH

Institute of Applied Chemistry
National Tsing-Hua University
Hsinchu, Taiwan 300
Republic of China

Received August 1, 1980; revised January 16, 1981