

STUDIES OF THE GAS PHASE AND Li/TiO₂ CATALYZED OXIDATIVE COUPLING OF METHANE

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ABSTRACT

The oxidative coupling of CH₄ was studied in the absence of catalysts and using a series of lithium-promoted TiO₂ catalysts by co-feeding CH₄ and O₂. Under some operating conditions, significant gas phase oxidative coupling can occur in the absence of catalysts. The general trend dictated by the gas phase kinetics is that the hydrocarbon selectivity falls as conversion increases. In the catalytic study, the degree of promotion was studied by varying the Li loading from 0 to 31.7% on the rutile phase of TiO₂. Generally, increasing the Li loading reduces the combustion capacity of the catalyst, lowers CH₄ conversion, and increases hydrocarbon selectivity. A 16.2% Li/TiO₂ catalyst had CH₄ conversions around 15% with hydrocarbon selectivities about 75% measured after 2 hours time-on-stream. X-ray diffraction, x-ray photoelectron spectroscopy, and differential thermal analysis were used to characterize the catalyst.

INTRODUCTION

Oxidative coupling of methane has been demonstrated using cyclic feeds(1-3), and co-feeding methane and oxygen (4-9), on a variety of metal oxide catalysts. Little attention has been paid to the gas phase reactions that can occur, even though it has been established that the mechanism involves the formation of CH₃ radicals. One of the objectives of the work reported here was to establish the role of the methane oxidative coupling gas phase reactions. The second objective was to determine the effect of Li on a lithium-titania catalyst system in relation to the gas phase results. The rutile phase of titania was chosen because our previous work indicated that the support imparted special oxygen transfer capacity to Pt supported on rutile (10). Lithium has been shown to be an effective promoter for the oxidative coupling of methane (6), and for this reason it was chosen to promote the titania catalysts. Characterization techniques involving XRD, XPS, and DTA were used to relate the role of Li with the activity results.

EXPERIMENTAL

A detailed description of the experimental apparatus has been presented elsewhere (11), thus only a brief description is given here. The activity measurements were carried out in a single pass flow reactor (0.95 O.D., 15 cm long) made of fused silica. A resistive furnace was specially designed to minimize non-isothermality. Experiments were also performed in a reactor filled with quartz chips and in a stainless steel reactor. Activity measurements were conducted by co-feeding methane, O₂ and He as a diluent. Typical operating conditions were as follows: i) temperature 600-800°C, ii) contact time 0.25 to 1.05 g s/ml, and iii) feed mole ratio of methane to oxygen of 2:1 to 37:1. The reactor effluent concentrations were measured by gas chromatography using carbosphere and Hayesep Q columns in parallel. A different reactor was used for each catalyst sample due to the apparent formation of lithium silicates on the reactor walls.

The catalyst were prepared by wet impregnation using Li₂O dissolved in deionized water to give lithium loadings of 0.0, 1.0, 3.8, 6.7, 11.0 16.2, and 31% on the rutile-titania support (12). XRD analysis was conducted using a Cu K-alpha radiation, and XPS analysis were conducted on a HP-5950 ESCA spectrometer with an Al anode.

RESULTS AND DISCUSSION

Conversion and selectivity (amount of methane converted to a product) results for the gas phase studies are shown in Figs. 1a and 1b at various reactant partial pressures and in Figs. 2a and 2b at various temperatures. Depending on operating conditions; gas phase results yielded selectivities varying from 65% at 2% conversion, to 29% at 32% conversion. Results obtained when the reactor was filled with quartz chips were similar to the gas phase results, indicating that the quartz reactor walls were not responsible for the gas phase results. However, activity measurements conducted in a stainless steel reactor resulted in 100% oxygen conversion and complete combustion of methane to CO₂.

It is clear from Figs. 1a and b and 2a and b that as conversion increases, selectivity to C₂ decreases. This trend is valid when other variables, such as contact time or oxygen and methane partial pressures, are changed, and it appears to be a generic relationship. A detailed comparison of the conversion versus selectivity in the gas phase and catalytic results has been made showing that about half of the published results are below our gas phase results, whereas the other half are above (11). This indicates that in some of the catalytic studies the catalysts promoted combustion of the gas phase products to CO₂.

Results obtained with a 1% Li catalyst are shown in Figs. 1c and 1d at various reactants partial pressures and in Figs. 1c and 2d at various temperatures. It can be seen that the catalyst promotes the combustion of C₂ and CO to CO₂. Under the various conditions shown in Fig. 1-2, c-d, the C₂ yield obtained in the presence of the 1% Li/TiO₂ catalyst is lower than in the gas phase.

Figures 3(a) to 3(c) display conversion, selectivity, and yield (conversion times selectivity), obtained with catalysts with different Li loadings, with a Li/MgO catalysts, and without catalysts. The results were obtained under the same operating conditions consisting of 250 mg of sample, dilution ratio of 0.4 (to minimize gas phase results), 100 cc/min total feed flow rate, methane to oxygen feed ratio of 4, 800°C, and after 2 hrs. of time-on-stream. The results in Fig. 3 show that as Li loading increases up to 11%, oxygen conversion decreases leading to an increase in selectivity. Further addition of Li results in an increase in conversion and selectivity, resulting in the highest yield for the 16.2% catalysts. Past the 16% loading the conversion decreases again lowering the yield.

XPS and XRD analysis have been conducted on the 16% catalysts at room temperature. However, DTA analysis indicates that there is a phase transition at about 750°C; consequently, the results at room temperature might not be relevant at the reaction conditions. The room temperature results indicate that increasing Li loading decreases the concentration of surface oxygen which is responsible for the oxidation of reaction intermediates. Work is underway to characterize the catalyst at reaction conditions, and ascertain the nature of the surface species responsible for the increase in selectivity.

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REFERENCES

1. Keller, G. E., and Bhasin, M. J., *J. Catal.* **73**, 9-19 (1982).
2. Labinger, J. A., and Ott, K. C., *J. Phys. Chem.* **91**, 2682-84 (1987).
3. (a) Sofranko, J. A., Leonard, J. J., and Jones, C. A., *J. Catal.* **103**, 302-10 (1987). (b) Jones, C. A., Leonard, J. J., and Sofranko, J. A., *J. Catal.* **103**, 311-19 (1987).
4. (a) Aika, K.-I., T. Moriyama, N. Takasaki, and E. Iwamatsu, *J. Chem. Soc., Chem. Commun.* 1210-11 (1986).
5. Hinsen, W., W. Bytyn, and M. Baerns, 8th Int. Cong. on Catal. Proc. III, 581-92 (1984).
6. Ito, T., J.-X. Wang, C.-H. Lin, and J. H. Lunsford, *J. Am. Chem. Soc.* **107**, 5062-68 (1985).
7. Kimble, J. B., and J. H. Koltz, *Energy Prog.* **6**, 226-29 (1986).
8. (a) Lin, C.-H., K. D. Campbell, J.-X. Wang, and J. H. Lunsford, *J. Phys. Chem.* **90**, 534-37 (1986). (b) Lin, C.-H., T. Ito, J.-X. Wang, and J. H. Lunsford, *J. Am. Chem. Soc.* **109**, 4808-10 (1987).
9. (a) Otsuka, K., Q. Liu, M. Hatano, and A. Morikawa, *Chem. Lett.* 467-68 (1986). (b) Otsuka, K., Q. Liu, M. Hatano, and A. Morikawa, *Chem. Lett.* 903-06 (1986). (c) Otsuka, K., K. Jinno, and A. Morikawa, *J. Catal.* **100**, 353-59 (1986).

10. Lane G. S., and E. E. Wolf, *J. Catal.* **105**, 386-404 (1987).
11. Lane G. S., and E. E. Wolf, *J. Catal.* In press.
12. Lane G. S., and E. E. Wolf, *Proc. 9th Int. Congress on Catalysis, Calgary* (1988).

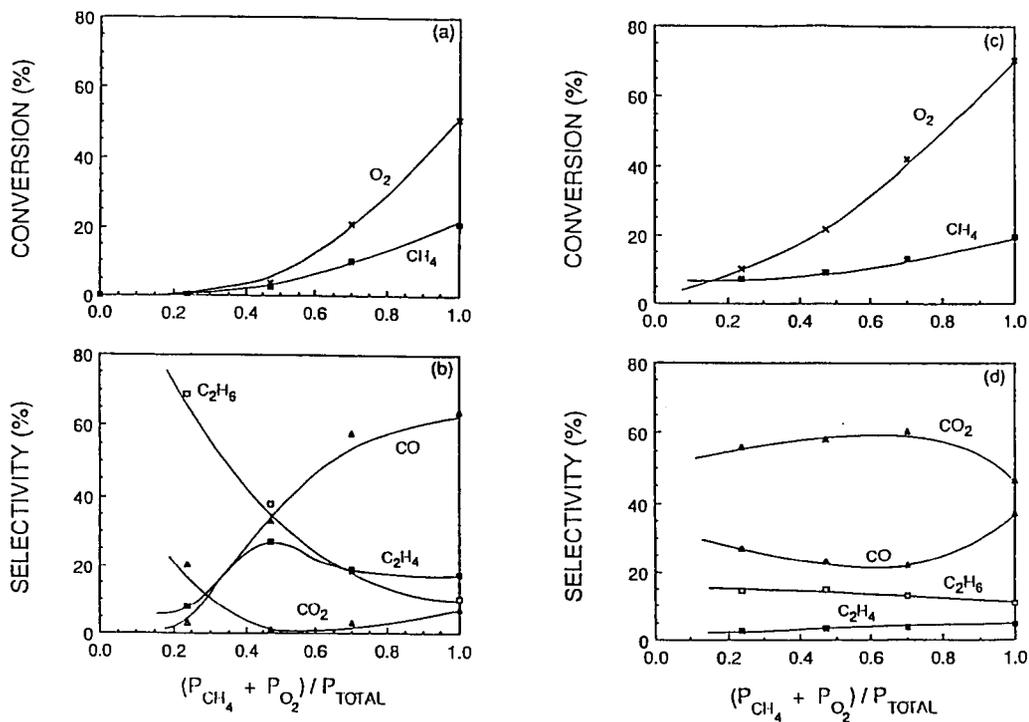


Fig. 1. Effect of dilution on conversion and selectivities at 750°C with a CH₄/O₂ feed mole ratio of 2 and a total flow rate of 50 cc/min. (a) and (b) represent results from a homogeneous study, and (c) and (d) represent results for a 1.0% Li/titania catalyst (250 mg sample).

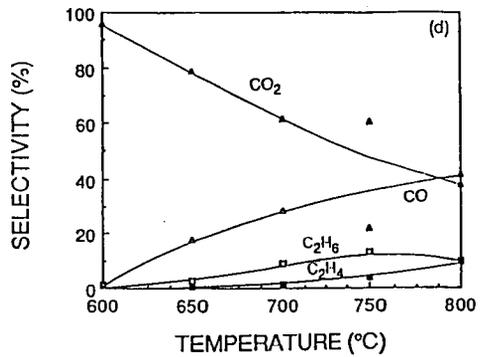
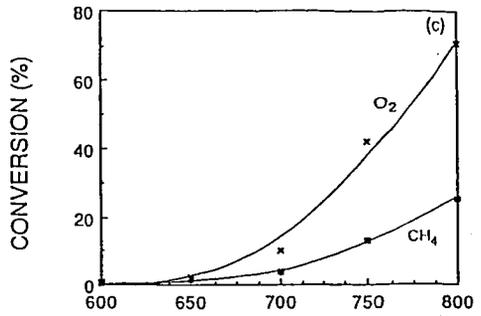
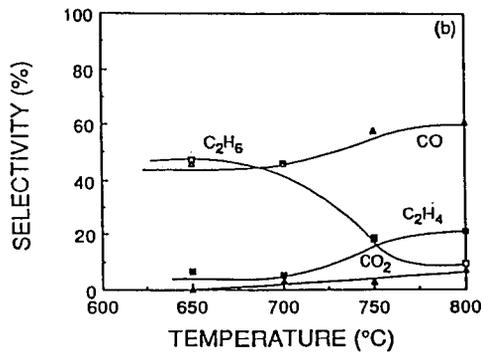
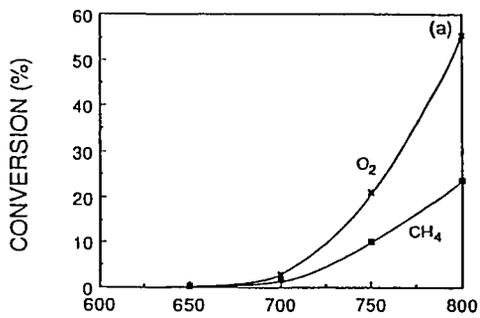


Fig. 2. Comparison of the effects of temperature on conversion and selectivity for a feed flow rate of 50 cc/min, CH₄ and O₂ partial pressures of 0.47 and 0.23, and a dilution ratio of 0.7. (a) and (b) represent results from a homogeneous study, and (c) and (d) represent results for a 1.0% Li/titania catalyst (250 mg sample).

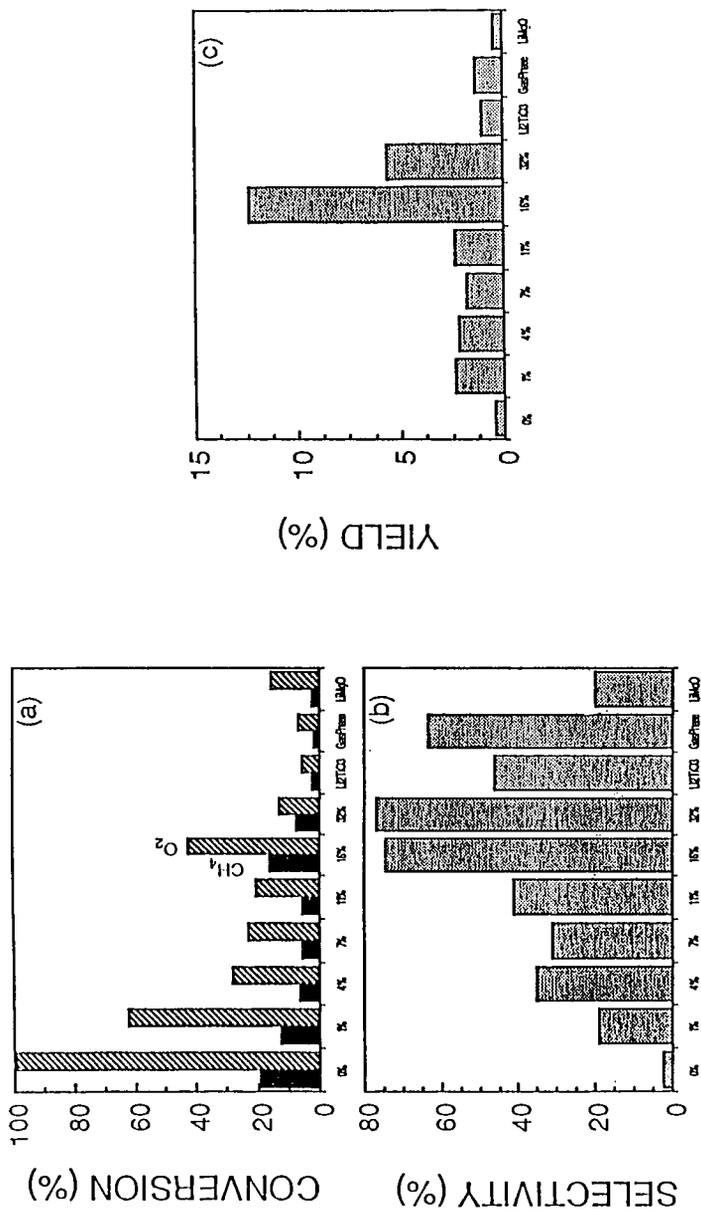


Fig. 3. Comparison of conversions, selectivities, and yields of several catalysts. The results represent samples taken at 800°C and 2 hours time-on-stream with a CH_4/O_2 feed mole ratio of 4, a total flow rate of 100 cc/min, a 250 mg catalyst sample, and a reactant partial pressure of 0.4.