8686 J. Phys. Chem. 1992, 96, 8686-8688

(16) Miller, R.; Lunkenheimer, K. *Colloid Polym. Sci.* **1986**, *264*, 273.
(17) Lunkenheimer, K.; Miller, R. *J. Colloid Interface Sci.* **1987**, *120*, 176.
(18) Lunkenheimer, K.; Pergande, H.-J.; Krüger, H. *Rev. Sci. Instrum.* **1987**, *58*, 2313.
(19) Lunkenheimer, K.; Haage, K.; Miller, R. *Colloids Surf.* **1987**, *22*, 215.
(20) Lunkenheimer, K.; Miller, R. *Abh. Akad. Wiss. DDR*, **1986**, **1987**, *Nr. 1N*, 113.
(21) Hommelen, J. R. *J. Colloid Sci.* **1959**, *14*, 385.
(22) Davies, J. T.; Rideal, E. K. *Interfacial Phenomena*; Academic Press: New York, 1963.
(23) Shinoda, K.; Nakagawa, T.; Tamamushi, B. I.; Isemura, T. *Colloidal Surfactants*; Academic Press: New York, 1963.
(24) Defay, R.; Prigogine, I.; Bellemans, A.; Everett, D. H. *Surface Tension and Adsorption*; Longmans, Green and Co. Ltd.: London, 1966.
(25) Vochten, R.; Petre, G. *J. Colloid Interface Sci.* **1973**, *42*, 320.
(26) Lucassen-Reynders, E.-H. In *Anionic Surfactants—Physical Chemistry of Surfactant Action*; Lucassen-Reynders, E.-H., Ed.; Marcel Dekker: New York, 1981; Vol. 11, p 1.
(27) Schulze, U. *Mehrphasenregression*; Akademie-Verlag: Berlin, 1987.
(28) Marquardt, D. W. J. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431.
(29) Betts, J. J.; Pethica, B. A. *Proceedings of the 2nd International Congress on Surface Active Substances*; London, 1957; p 152.
(30) Prigogine, I.; Defay, R. *Chemische Thermodynamik*; VEB Deutscher Verlag für Grundstoffindustrie: Leipzig, 1962.
(31) Baret, J. In *Progress in Surface and Membrane Science*; Cadenhead, D. A., Danielli, J. F., Eds.; Academic Press: New York, 1981; Vol. 14, p 291.
(32) Lunkenheimer, K.; Hirte, R. Lectures held at VIIth Int. Conf. Surf. Act. Subst., Bad Stuer, Germany, 1988; 10th European Conference "Chemistry of Interfaces", San Benedetto, Italy, 1988; 11th European Conference "Chemistry of Interfaces", Strausberg (Berlin), Germany, 1990.
(33) Lunkenheimer, K.; Hirte, H. Manuscript in preparation.

Low-Temperature Catalytic Selective Partial Oxidation of Methane to CO and H_2 over Ni/Yb_2O_3

Vasant R. Choudhary,* Amarjeet M. Rajput, and Vilas H. Rane

Chemical Engineering Division, National Chemical Laboratory, Pune 411 008, India *(Received: April 24, 1992; In Final Form: July 14, 1992)*

Ni/Yb_2O_3 showed high activity/selectivity in catalytic oxidative conversion of methane to CO and H_2 at low temperatures (300–700 °C) and extremely high space velocity (5×10^5 $cm^3 \cdot g^{-1} \cdot h^{-1}$) at atmospheric pressure. The low-temperature catalytic process operates far away from the thermodynamic equilibrium and also follows a reaction path totally different from that considered for the high-temperature noncatalytic and catalytic processes. The formation of surface carbon species in the initial reaction period seems to play an important role in the catalytic process.

Syngas is produced from methane mostly by steam reforming,[1,2] which suffers from severe limitations, viz., very high energy requirements, poor CO selectivity, and high H_2/CO ratio unsuitable for methanol and Fischer–Tropsch synthesis. It can also be produced by noncatalytic oxidation of methane[1,2] but, although this process is free from the above limitations, it operates at very high temperatures (>1300 °C). In recent studies, the use of $Ln_2Ru_2O_7$ (Ln = lanthanide)[3] and $Eu_2Ir_2O_7$,[4] operating at 770 °C, and $Ni–Al_2O_3$,[5] operating at 800–900 °C and extremely low space velocity, in the oxidative methane-to-syngas conversion at 1 atm with an establishment of thermodynamic equilibrium, has been reported. The reaction path for these high-temperature noncatalytic/catalytic processes involves combustion of a part of CH_4 to CO_2 and H_2O with complete O_2 conversion followed by methane, steam, and CO_2 reforming and reverse shift reactions leading to the equilibrium product distribution.[1,3–6] The catalytic oxidation process will be commercially more feasible if operated at low temperatures (below 700 °C) because it is extremely difficult to operate the process at high temperature (>700 °C). However, at low temperatures (<700 °C) the equilibrium CO selectivity is very poor.[3,5] It is, therefore, of great interest and practical importance to have a catalytic process operating at lower temperatures but far away from the equilibrium so that high selectivity could be achieved.

We report here our preliminary results showing high conversion/selectivity and space–time yield (STY) in the catalytic oxidation of methane to CO and H_2 or syngas (which follows a reaction path totally different from that involved in the earlier high-temperature noncatalytic and catalytic processes) over Ni/Yb_2O_3 at low temperature (300–700 °C) and atmospheric pressure.

The NiO/Yb_2O_3 catalysts were prepared by thoroughly mixing finely ground Yb_2O_3 (99.95%, Aldrich) and nickel nitrate (Loba, GR) in the required proportions with deionized water to form a thick paste, drying and decomposing in air at 600 °C for 4 h and then powdering, pressing binder-free, crushing to 22–30 mesh size particles, and calcining in air at 900 °C for 6 h. The reactions were carried out in a quartz microreactor (i.d. 4 mm) containing 20 mg of catalyst, pretreated in situ at 900 °C in a flow of moisture-free N_2 for 1 h. The microreactor was operated in both continuous and pulse reaction modes. Data on both the reduced [by H_2 at 500 °C for 1 h] and unreduced catalysts (i.e. Ni/Yb_2O_3 and $NiO \cdot Yb_2O_3$, respectively) have been collected. The reaction temperature was measured by a chromel–alumel thermocouple located in the catalyst bed. The exothermic heat of reaction, particularly at lower temperatures (⩽600 °C) was removed by passing air around the reactor; there was no hot spot in the catalyst bed. The catalyst was reduced by H_2 in a flow [1.3 $cm^3 \cdot s^{-1}$] of 20% H_2 (balanced N_2) at 500 °C for 1 h. The space velocity was measured at STP. The catalytic reactions in the continuous microreactor were carried out under steady-state condition for a period of about 1 h before the data was collected for each run; the duration of the run was about 1.5 h. The pulse reactions at different temperatures were carried out by injecting a pulse of reactant(s) in the microreactor after it attained the required temperature, whereas the pulse experiments at the same temperature were carried out by injecting a number of pulses of the reactant(s), one after another, at an interval of about 15 min. The reaction water from products was condensed at 0 °C. The feed and products were analyzed by an on-line gas chromatograph. The C, H, and O balances were better than 95%.

The results (Table I) reveal the possibility of oxidative conversion of methane to syngas (H_2/CO = 2.0) over the catalysts at ⩽700 °C (even at 300 °C) with high conversion, very much higher selectivity than that can be achieved at the equilibrium[5] and much higher STY than that was obtained earlier.[3–5] The equilibrium CO selectivity at 700, 600, 500, 400, and 300 °C is about 92, 67, 25, 4.5%, and negligibly small, respectively.[5]

0022-3654/92/2096-8686$03.00/0

TABLE I: Oxidative Conversion of Methane over the Catalysts[a]

catalyst	temp[b] (°C)	CH_4 conversion (%)	selectivity (%) H_2	selectivity (%) CO	H_2/CO ratio	CO STY ($mol{\cdot}g^{-1}{\cdot}h^{-1}$)
Yb_2O_3	700	no reaction				
Ni/Yb_2O_3 (Ni/Yb = 0.1)	500	no reaction				
	700	68.4	85.2	94.4	1.85	10.0
	500	62.2	82.1	92.3	1.78	8.93
	300	56.0	80.0	88.8	1.80	7.73
Ni/Yb_2O_3 (Ni/Yb = 1.0)	400	no reaction				
	500	76.1	88.6	89.1	2.00	10.5
	700	85.7	94.2	94.4	2.00	12.5
	500	76.7	88.1	88.9	1.98	10.5
	400	73.0	86.3	86.2	2.00	9.7
Ni/Yb_2O_3 (Ni/Yb = 4.0)	400	no reaction				
	500	76.3	93.1	88.0	2.12	10.4
	700	86.6	96.1	95.5	2.01	12.9
	500	75.6	93.2	89.2	2.09	10.5
	300	70.9	87.0	83.6	2.08	9.2
NiO/Yb_2O_3 (Ni/Yb = 1.0)	500	no reaction				
	600	79.1	91.6	93.0	1.97	11.4
	700	84.9	95.7	95.2	2.01	12.6
	500	74.0	90.0	89.8	2.00	10.3
	300	71.1	87.9	84.4	2.08	9.3

[a] Feed, 67 mol % CH_4 and 33 mol % O_2; space velocity (SV), 5.2×10^5 $cm^3{\cdot}g^{-1}{\cdot}h^{-1}$; and pressure, 1.0 atm. [b] Data at different temperatures were collected following the temperature sequence.

The catalyst prereduction was not essential but the unreduced catalyst showed activity only at $\geq$550 °C; during the reaction at $\geq$550 °C, the catalyst is reduced by the H_2 formed and then showed activity at <550 °C, indicating that the catalyst is active/selective only in its reduced form. The results of the pulse reaction of methane in absence and presence of free O_2 over the NiO/Yb_2O_3 and Ni/Yb_2O_3 (Figure 1) are consistent with the above. The pulse reaction was carried out at higher pressure (1.8 atm) and also at lower gas velocity (90 000 $cm^3{\cdot}g^{-1}{\cdot}h^{-1}$) than that employed for the continuous reaction. Since the reaction is not thermodynamically favored at higher pressure,[5] the CO selectivity obtained in the pulse reaction is expected to be smaller (Figure 1, Table I).

The facts that even the prereduced catalyst showed activity at <500 °C only after its use in the reaction at $\geq$500 °C (Table I) and also showed higher selectivity in the pulse reaction at 500 °C after a number of pulses at 700 °C (Figure 1c) indicate creation of active sites responsible for the low-temperature activity/selectivity due to further catalyst reduction and/or formation of surface carbon species.

In the pulse reaction of O_2 (at 700 °C) over the catalyst in the continuous oxidative methane conversion and also over the catalyst in the pulse reaction (by injecting three pulses of methane in presence of free O_2 at 700 °C), the formation of CO and CO_2 to a significant extent was observed. This reveals the presence of surface carbon species on the catalyst, probably due to the following reactions

$$2CO \rightleftharpoons CO_2 + C(ads)$$

$$CO + H_2 \rightleftharpoons H_2O + C(ads)$$

In the reaction of methane with CO_2 (CH_4/CO_2 = 1.0) or steam (H_2O/CH_4 = 1.0) over the Ni/Yb_2O_3 (at $\leq$500 °C and SV = 5×10^5 $cm^3{\cdot}g^{-1}{\cdot}h^{-1}$), the methane conversion was negligibly small. This reveals that the reaction path for the low-temperature catalytic process is completely different from that considered for the earlier high-temperature noncatalytic and catalytic processes.[1,3,5] The low-temperature process probably involves heterolytic dissociation of methane to CH_3^- and H^+ on the acid–base pair of the low coordinated surface of the rare earth oxide[7,8] and oxidation of CH_3^- by O_2 to OCH_3^- which is decomposed to CO and H_2 and/or oxidized to $HCOO^-$ leading to CO, H_2, and CO_2 (probably on Ni), similar to that observed for low-temperature oxidation of preadsorbed CH_4 on MgO.[8] However, this is speculation and further work is necessary for understanding the reaction mechanism.

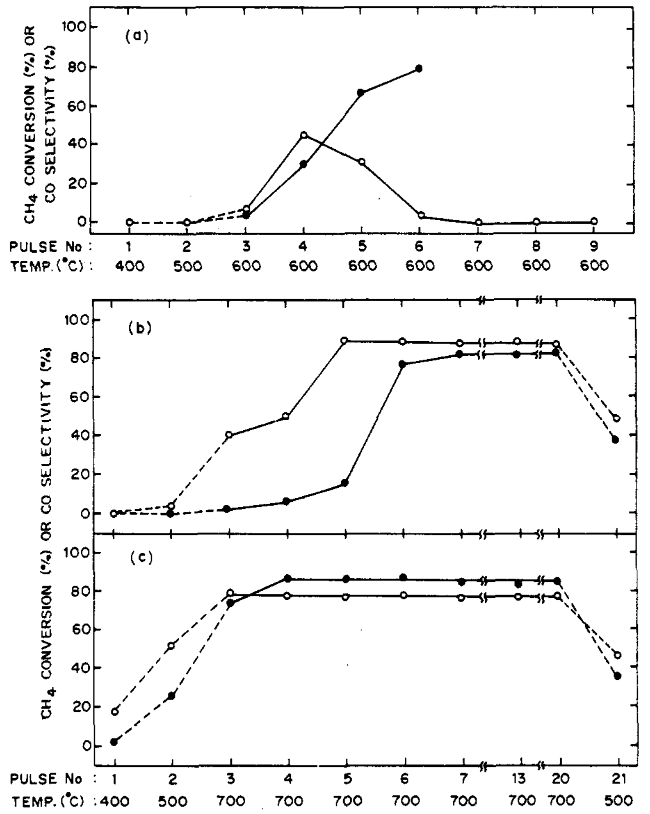

Figure 1. Influence of pulse number and temperature on CH_4 conversion (○) and CO selectivity (●) in pulse reaction of (a) pure methane on NiO/Yb_2O_3 and of a mixture of 67 mol % CH_4 and 33 mol % O_2 over (b) NiO/Yb_2O_3 and (c) Ni/Yb_2O_3 [Ni/Yb mole ratio = 1.0]. Reaction conditions: amount of catalyst, 20 mg; carrier gas (He) flow rate, 30 $cm^3{\cdot}min^{-1}$; pulse size, 1.0 cm^3; pressure, 1.8 atm.

Registry No. Ni, 7440-02-0; Yb_2O_3, 1314-37-0; CH_4, 74-82-8; H_2, 1333-74-0; CO, 630-08-0.

References and Notes

(1) Kirk, R. E., Othmer, D. E., Eds. *Encyclopedia of Chemical Technology*, 3rd ed.; Wiley Interscience: New York, 1980; Vol. 12, pp 938–982.

(2) *Ulman's Encyclopedia of Industrial Chemistry*, 5th revised ed.; VCH Verkagsgesettschaft mbh: Weinheim, 1989; Vol. A 12, pp 169–306.

(3) Ashcroft, A. T.; Cheetham, A. K.; Foord, J. S.; Green, M. L. H.; Grey,

C. P.; Murrel, A. J.; Vernon, P. D. F. *Nature* **1990**, *344*, 319-321.

(4) Jones, R. H.; Ashcroft, A. T.; Waller, D.; Cheetham, A. K.; Thomas, J. M. *Catal. Lett.* **1991**, *8*, 169-174.

(5) Dissanayake, D.; Rosynek, M. P.; Kharas, K. C. C.; Lunsford, J. H. *J. Catal.* **1991**, *132*, 117-127.

(6) Prettre, M.; Eichner, C.; Perrin, M. *Trans. Faraday Soc.* **1946**, *43*, 335-340.

(7) Choudhary, V. R.; Rane, V. H. *J. Catal.* **1991**, *130*, 411-422.

(8) Ito, T.; Watanabe, T.; Tashiro, T.; Toi, K. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 2381-2395.

High-Resolution Stimulated Brillouin Gain Spectroscopy of Liquid Benzene Shows No Evidence of a "Structural Transition"

W. Tandy Grubbs and Richard A. MacPhail*

Department of Chemistry, P. M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706

(Received: June 29, 1992; In Final Form: September 8, 1992)

We have used high-resolution stimulated Brillouin gain spectroscopy to search for evidence of a "structural transition" within the liquid phase of benzene. On the basis of previous measurements of depolarized light scattering intensities and Brillouin line shifts, it has been proposed that such a transition occurs in the temperature range 42–48 °C (Rozhdestvenskaya, N. B.; Smirnova, L. V. *J. Chem. Phys.* **1991**, *95*, 1223). Our highly accurate Brillouin shift measurements show a linear dependence on temperature from 24 to 69 °C, with no sign of any anomaly.

Introduction

It has recently been proposed that there exists within the liquid phase of benzene a "structural transition" involving different local packing arrangements of the benzene molecules.[1,2] While the possibility of different favored orientational packing arrangements in liquid benzene is well recognized,[3-9] the idea that competition between these arrangements could lead to a well-defined transition over a fairly narrow temperature range is probably surprising to many. Indeed, developing the correct interpretation of such a transition would present a considerable challenge. Before taking on this challenge, it is important to establish through further experiments whether this structural transition in fact exists. In this Letter we contribute to this effort through a high-resolution stimulated Brillouin gain study of liquid benzene.

Rozhdestvenskaya and Smirnova first suggested the existence of a structural transition in liquid benzene on the basis of measurements of the integrated depolarized light scattering intensity, a quantity sensitive to orientational correlations in the fluid.[1] They observed an increase in the scattering intensity as the temperature was raised from 7 to 65 °C, with two anomalous regions: the first corresponding to a break in slope between 27 and 30 °C and the second to a significant rise and fall in the intensity between 42 and 48.5 °C. Letamendia et al.[10] have reported significant changes in the Brillouin line shift and Landau–Plazeck ratio of liquid benzene in the same 42–48 °C region. Pinan–Lucarre et al.[11] examined the second moment of the depolarized Rayleigh wing intensity of benzene and found a break in the temperature dependence near 40 °C, but they observed no unusual temperature behavior in the integrated intensity of the "forbidden" Raman band at 405 cm^{-1}. Rhozhdestvenskaya and Smirnova have also reported "transition" behavior in the integrated depolarized light scattering intensity of liquid hexafluorobenzene.[2] The temperature dependence they observe for hexafluorobenzene is surprisingly similar to that seen in benzene, including a break in slope between 20 and 30 °C and a "transition" between 42 and 50 °C, except that the sign of the temperature dependence is reversed (i.e., the intensity decreases with increasing temperature).

The technique employed here, continuous-wave (CW) stimulated Brillouin gain (SBG) spectroscopy, has recently been shown to be an effective way to obtain high-resolution Brillouin spectra of gases,[12] liquids,[13,14] and solids.[15] In this experiment, two CW laser beams, one from a tunable pump laser and one from a weaker probe laser, are crossed in the sample. When the difference in the frequencies of these two beams $\Omega = \omega_2 - \omega_1$ is equal to the Brillouin frequency, acoustic waves with wavevector $\mathbf{k} = \mathbf{k}_2 - \mathbf{k}_1$ are stimulated in the sample, and energy is transferred from the higher frequency laser beam to the lower frequency one through Brillouin-induced four-wave mixing.[16] The SBG spectrum is collected by scanning the frequency of the pump beam and monitoring the gain (or loss) in the probe beam power as a function of Ω. The gain can be related to the spectral density $S(k,\Omega)$ measured in a spontaneous Rayleigh–Brillouin experiment[17] through the expression[16]

$$G(k,\Omega) = \eta(4\pi^3 c\omega_2/\omega_1^3)(N/k_BT)(d\sigma/d\Omega)[\Omega S(k,\Omega)]P(\omega_2) \tag{1}$$

where G is the gain or fractional change in the probe power at the laser difference frequency Ω, η is the crossing efficiency for the two beams, ω_1 and ω_2 are the frequencies of the probe and pump beams, respectively, N is the number density of the medium, k_BT is the thermal energy, $d\sigma/d\Omega$ is the scattering cross section, and $P(\omega_2)$ is the power of the pump beam.

Several features of CW SBG spectroscopy make it particularly attractive for the problem at hand. First, extremely high-resolution SBG spectra can be obtained by employing narrow line width CW lasers. Perhaps more importantly, measurements of the Brillouin shifts and line widths can be made with high accuracy and precision since the frequency scale corresponds to the difference between two stabilized laser frequencies. However, because of the additional Ω factor multiplying $S(k,\Omega)$ in the square brackets in eq 1, the Rayleigh peak is suppressed and the Landau–Plazeck ratio cannot be determined from the SBG spectrum.

Experimental Section

Our SBG spectrometer has been described in detail previously.[13,14] A frequency-stabilized ring dye laser (Coherent CR-699-29) provides a tunable pump beam with 100 mW of power at 633 nm, and a frequency-stabilized HeNe laser (Laboratory for Science Model 200) provides a 1-mW probe beam with low amplitude noise. The vertically polarized pump and probe beams are loosely focused and crossed within the sample cell. Balanced detection and double modulation are employed to enhance the signal-to-noise.[13,14] For the spectra reported here, the scattering angle was 178.7°, the time constants for the pre- and postfilters on our lock-in amplifier (Stanford Research Systems SR510) were set to 0.1 and 1 s, respectively, and the dye laser scan speed was

0022-3654/92/2096-8688$03.00/0 © 1992 American Chemical Society