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NICKEL(II) MOLYBDATE ($NiMoO_4$) AS METHANATION CATALYSTS

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ABSTRACT

Three $NiMoO_4$ catalysts, on Al_2O_3 and SiO_2–Al_2O_3 supports, were evaluated for use as methanation catalysts using the DTA technique. All three catalysts were effective for the methanation reaction, although they rapidly developed carbon deposits at the H_2:CO ratios and flow-rates employed.

INTRODUCTION

One of the most important problems for large scale solar energy utilization is the development of a suitable energy transmission system from the solar energy collector to a suitable electric power generator or storage facility. Of the many energy transmission systems proposed, the cyclic catalytic reaction of methane (CH_4) and steam merits further investigation[1]. This system is based upon the reaction:

$$CH_4(g) + H_2O(g) \underset{\text{cata.II}}{\overset{\text{cata.I}}{\rightleftarrows}} CO(g) + 3H_2(g) \tag{1}$$

The reaction from left to right is the well known "reforming" reaction while that from right to left is part of the Fischer–Tropsch system, or more specifically, the methanation reaction. Both reactions are well known from an industrial viewpoint, although new catalysts, such as catalysts I and II, are constantly being evaluated.

Of interest here is the use of nickel molybdate ($NiMoO_4$) catalysts for the methanation reaction. In order to evaluate these catalysts, a DTA method was employed which permitted a rapid screening procedure, plus some measure of the usefulness of the catalyst for the methanation reaction. The use of DTA and DSC for the evaluation of methanation catalysts has been discussed by Beecroft et al.[2], and the procedure used here is similar to the one that those authors employed. Three catalysts were evaluated: two catalysts were $NiMoO_4$ on an Al_2O_3–SiO_2 support and one was $NiMoO_4$ on an Al_2O_3 support.

EXPERIMENTAL

Catalysts

The three catalysts used were obtained from the Climax Molybdenum Co., Ann Arbor, MI. Their composition and specifications were as follows:

(a) $NiMoO_4$ on Al_2O_3; Lot No. 1104-110; 169 m^2 g^{-1} surface area; Harshaw AL-140P support; 9.5% Mo, 5.9% Ni, Ni/Mo = 0.986:1.

(b) $NiMoO_4$ on Al_2O_3–SiO_2; Lot No. 1120-135; 159 m^2 g^{-1} surface area; Harshaw AL-1602T support (1/8 in. tablets), 91% Al_2O_3–6% SiO_2; 8.54% Mo, 5.15% Ni, Ni/Mo = 0.986:1.

(c) $NiMoO_4$ on Al_2O_3–SiO_2; Lot No. 1164-33; 113 m^2 g^{-1} surface area; Harshaw AL-1605P support, 91% Al_2O_3–6% SiO_2; 21.0% Mo, 11.7% Ni, Ni/Mo = 0.91:1.

DTA apparatus

The DTA apparatus was conventional in design[3]. It used small stainless-steel cups to contain the sample and reference materials with sensing thermocouples spot-welded to the base of each cup. A heating rate of 10°C min^{-1} was employed and the variable gas-flow rate and mixing were controlled by a Matheson R7 300 Series gas proportioner. The ratios of gas-flow rates of H_2:CO used were 1:1, 1:2, and 2:1. Many other flow-rates were evaluated but only those listed above are reported here. The hydrogen and carbon monoxide gases were obtained directly from cylinders and were not subjected to purification. After passing through the gas proportioner, the gas mixtures entered the top of the furnace chamber and were immediately in contact with the sample and reference materials. The effluent gases excited at the bottom of the furnace chamber and were exhausted to the atmosphere.

RESULTS AND DISCUSSION

The rate of the methanation reaction, r, has been discussed by Beecroft et al.[2] using DSC parameters. Using a similar approach, but substituting DTA parameters, the rate of the methanation reaction at temperature T is proportional to R(dH/dT). The term, R(dH/dT), is the expression for the instantaneous rate of heat generation[4], and is given by the[4] equation:

$$\mathrm{R}\left(\frac{\mathrm{d}H}{\mathrm{d}t}\right) = (T_s - T_r) + \mathrm{R}(C_s - C_r) + \mathrm{R}C_s\mathrm{d}\frac{(T_s - T_r)}{\mathrm{d}t}$$

where T_s is the sample (and container) temperature; T_r is the reference (and container) temperature; C_s and C_r are the heat capacities of the sample and reference, respectively; $\mathrm{d}T_R/\mathrm{d}t$ is the heating rate; and R is a constant. The rate, r_T, is given by:

$$r_T = -\left(\frac{\mathrm{d}P_{\mathrm{CO}}}{\mathrm{d}t}\right)_T = \mathrm{a}\left[\mathrm{R}\left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\right]_T$$

where a is a constant. The rate of reaction is given by the rate expression:

$$r = -\left(\frac{dP_{CO}}{dt}\right) = K\,P_{CO}^{n}\,P_{H_2}^{m}\exp\left(-E/RT\right)$$

Experiments were carried out[2] with various partial pressures of CO and H_2 at differential flow-rates. From these data, Arrhenius plots could be made for the various catalysts used in the methanation reaction. No activation energies, E, however, were reported.

The DTA curves for the three catalysts used in these investigations are given in Figs. 1–3.

All of the DTA curves showed that $NiMoO_4$ catalyzed the methanation reaction, as given in eqn. (1). Since the reaction is highly exothermic, $\Delta H_{500} = -218$ kJ mole^{-1}, all of the curve peaks are exothermic and are very large in magnitude. The initial deviation from the baseline varies with change in composition (H_2:CO ratio), flow-rate and composition of the catalyst. Also, the curve peak maxima vary with the same parameters. They tend to be largest with the greatest flow-rate but there are some exceptions, for example, $NiMoO_4$ on Al_2O_3–SiO_2 (Lot No. 1120–135) (see Fig. 1).

The initial curve deviations (T_i) and peak maxima temperatures (ΔT_m) are listed in Table 1. As shown by the data, the T_i values tend to decrease with an increase

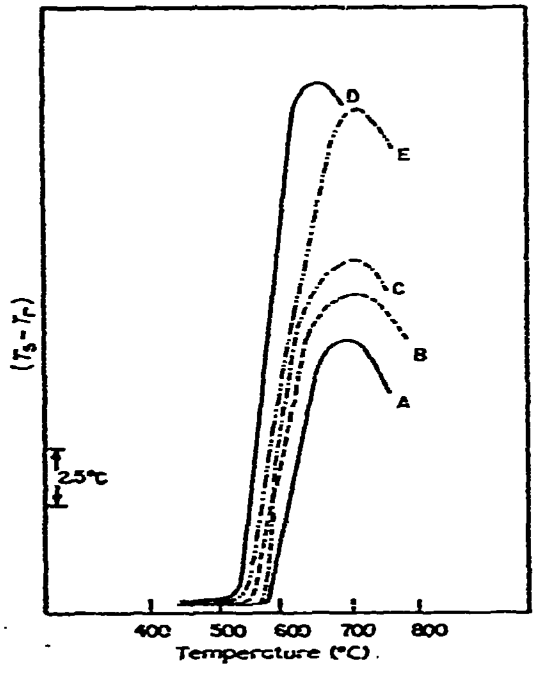

Fig. 1. Methanation reaction on $NiMoO_4$ (Al_2O_3–SiO_2) catalyst (Lot no. 1120–135). (A) 10:10 ml min^{-1}; (B) 20:20 ml min^{-1}; (C) 30:30 ml min^{-1}; (D) 40:40 ml min^{-1}; (E) 50:50 ml min^{-1}; (H_2:CO).

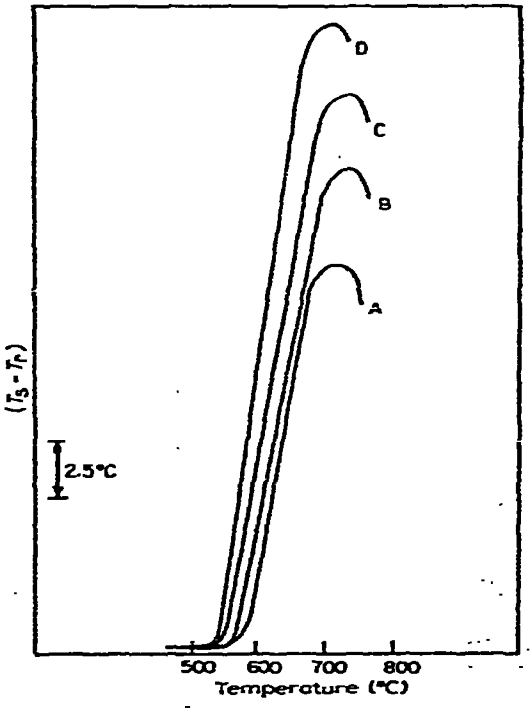

Fig. 2. Methanation reaction on $NiMoO_4$ (Al_2O_3) catalyst (Lot no. 1104–110). (A) 10:20 ml min^{-1}; (B) 20:40 ml min^{-1}; (C) 30:60 ml min^{-1}; (D) 40:80 ml min^{-1}; (H_2:CO).

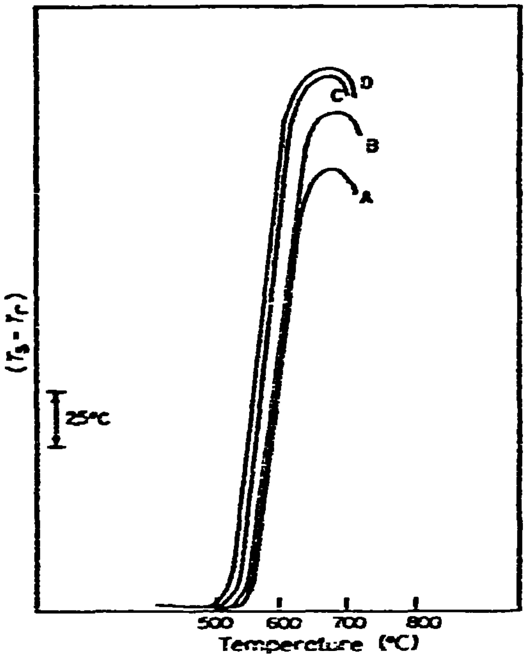

Fig. 3. Methanation reaction on $NiMoO_4$ (SiO_2–Al_2O_3) (Lot no. 1164-33). (A) 20:10 ml min^{-1}; (B) 40:20 ml min^{-1}; (C) 60:30 ml min^{-1}; (D) 80:40 ml min^{-1}; (H_2:CO).

TABLE I

CATALYST T_i AND ΔT_m VALUES

Flow-rate	*$NiMoO_4$ catalyst (°C)*		
H_2:CO (ml min^{-1})	*No. 1120-135*	*No. 1140-110*	*No. 1164-33*
10:10	569[a] 697[b]		
20:20	541 706		
30:30	564 702		
40:40	508 654		
50:50	515 711		
10:20		560 716	
20:40		550 737	
30:60		532 735	
40:80		528 709	
20:10			532 685
40:20			518 692
60:30			508 687
80:40			504 687

[a] T_i temperatures.

[b] ΔT_m temperatures.

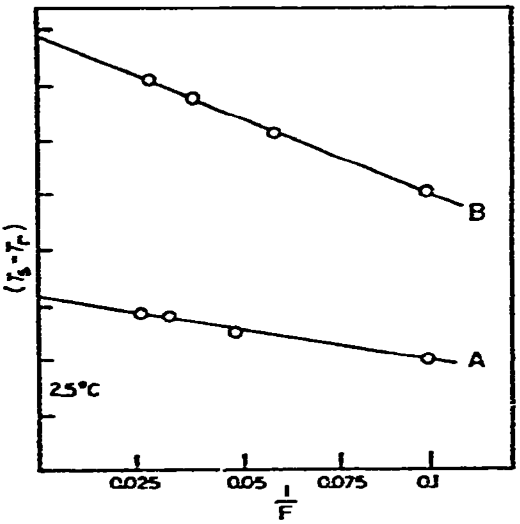

Fig. 4. Flow-rate for $NiMoO_4$ on Al_2O_3 (Lot No. 1104-110).

in flow-rate for each H_2:CO ratio and catalyst composition. The same appears to be true in the case of ΔT_m values.

The complicating factor with all of the catalyst composition and H_2:CO ratios was the deposition of carbon. All of the catalysts were black in color at the termination of the DTA run, which necessitated the use of fresh catalyst for each run. Unless a specific H_2:CO or flow-rate would prevent the carbon formation, the catalysts would not be very effective in cyclic catalytic systems, such as that illustrated in eqn. (1).

The effect of flow-rate of the reactant gases on the $(T_s - T_r)$ values for one of the catalysts is given in Fig. 4. The catalyst, Lot No. 1104-110, gave straight line plots for the temperatures indicated, which can be extrapolated to zero flow-rate. The zero flow-rate data can be used to obtain E values[2] but the values obtained here did not yield a suitable Arrhenius plot.

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