JOURNAL OF CATALYSIS 46, 417–419 (1977)

Mischmetal–Nickel Alloys as Methanation Catalysts

A major source of energy in future years may be coal gasified with steam to produce a low heating value mixture of H_2, CO, and CO_2. This gas mixture can be converted to high Btu gas (1000 Btu/ft^3) through the methanation reaction, $3H_2 + CO = CH_4 + H_2O$. Since Sabatier and Sendirens (*1*) reported methanation over a nickel catalyst in 1905, a considerable amount of research has been conducted on the catalytic synthesis of methane from a mixture of carbon monoxide and hydrogen. The major catalyst for the methanation reaction has continued to be nickel metal because of its high activity, low cost, and high selectivity for the formation of methane (*2*).

Previous investigations have shown that certain rare earth transition metal intermetallics are capable of rapidly absorbing and desorbing large quantities of hydrogen under mild conditions of temperature and pressure (*3*). Kuijpers and Loopstra (*4*) showed that the absorbed hydrogen was in its more active atomic form and occupied interstitial sites. Because of these properties, mischmetal–nickel (MM–Ni) intermetallics were investigated as methanation catalysts.

Mischmetal–nickel alloys were prepared by arc-melting the metal constituents on a water-cooled copper hearth. All metal compositions are in wt%. An analysis of the mischmetal showed 67% Ce, 13% La, 9% Pr, and 11% Nd, with minor impurities of Fe (0.2%) and Mg (0.3%). The nickel metal had a purity of 99.95%.

The consolidated MM–Ni alloys were ground in air to minus 25 plus 80 mesh and bulk density measurements were obtained. A sample size of 1 cm^3 (~4.5 g) was loaded onto a layer of Pyrex[1] glass wool inside a 0.5-in. o.d. stainless steel steady flow reactor. The sample temperature was monitored with a 0.125-in. o.d. stainless steel sheathed thermocouple placed in the center of the sample bed. A constant temperature was maintained by employing a 3-in. diam by 8-in. long aluminum cylinder as a heat sink with holes drilled to accommodate the reactor, a control thermocouple, and two 0.5-in. diam × 6-in. long cartridge heaters.

Helium was used to flush the reactor before and during heating to 400°C. At this temperature the helium was replaced with a hydrogen–carbon monoxide synthesis gas which had a ratio of approximately 3:1, and the pressure was increased to 10 atm. After a reaction period of from 5 to 22 hr, the temperature was decreased and the synthesis gas space velocity was adjusted to 4000 hr^{-1} (STP) before activity measurements were taken.

A commercial nickel methanation catalyst, Harshaw No. 0302T (15% Ni on alumina), was sieved to minus 25 plus 45 mesh and a 1 cm^3 (1 g) sample was used for comparison purposes. The commercial supported nickel catalyst was reduced in hydrogen for 1 hr at 400°C before introducing synthesis gas.

Catalyst activity was monitored by analyzing the product gas for CO, CH_4, and CO_2 by gas chromatography with a Carbosieve B column. By accurately controlling inlet flow with a mass flowmeter, a carbon mass balance calculation gave total product

[1] Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

ISSN 0021-9517

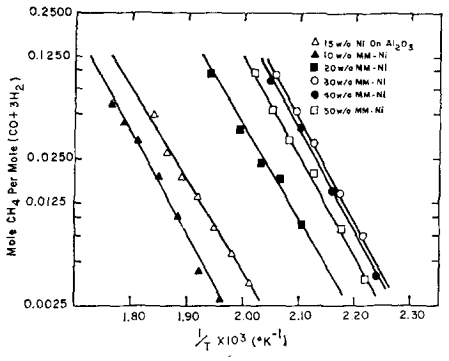

FIG. 1. Activity of mischmetal–nickel alloys as methanation catalysts at SV = 4000 hr^{-1}.

composition. Carbon found in the used catalyst introduced a small error in these calculations but it was determined to be less than 5% in the worst case. The exit gas composition was monitored for several days and data points were obtained while varying sample temperature. Low conversion to methane was maintained to prevent temperature "run away."

Total surface area determinations were obtained on the used samples with a gravimetric apparatus by the standard BET method after evacuation at 400°C for several hours and H_2 reduction at this temperature overnight. For measurement of active surface, chemisorption of CO was chosen rather than H_2 because of the hydrogen absorbing properties of the rare earth intermetallics. It is known, for example, that $LaNi_5$ can absorb hydrogen in interstitial sites in an amount exceeding that corresponding to $LaNi_5H_6$ (*5*). Chemisorption isotherms were determined at 0°C and CO pressures from 20 to 400 Torr. Formation of a monolayer was assumed to be complete at the lowest pressure of the straight line portion of the isotherm, which was generally about 100 Torr. Any problems of carbonyl formation are easily observed with the gravimetric absorption apparatus since formation of the volatile carbonyl results in a loss in sample weight on standing at 400 Torr CO pressure. No evidence of carbonyl formation was observed at 0°C.

During exposure to synthesis gas initially at 400°C, then in the range 200–250°C, the rare earth intermetallics underwent surprising changes. Surface areas increased from a few square centimeters per gram for the granular alloys to as high as 37 m^2/g in the case of the alloy containing 50% mischmetal. Total activity increased over a period of several hours to a constant very high level. X-Ray diffraction patterns for the as-prepared alloys showed a crystalline material with peaks identifying the expected intermetallic compounds, whereas the used catalysts were less crystalline and contained no intermetallics but gave patterns for rare earth oxide and Ni_3C. The mechanism of area formation is not completely known, and experimental work is continuing in this direction.

Figure 1 shows the relative activity of mischemetal–nickel alloys containing 10,

TABLE 1

Specific Activity of Various Methanation Catalysts

Catalyst (%)	BET area (m^2/g)	CO uptake (μmoles/g)	E_a (kcal/mole)	Turnover No.[a] @ 275°C × 10^3
Harshaw No. 0302T	77.6	177	27.6 ± 0.3	13
10 MM–Ni	1.3	9	29.1 ± 1.7	32
20 MM–Ni	20.1	87	27.9 ± 1.5	65
30 MM–Ni	30.0	286	32.4 ± 0.5	150
40 MM–Ni	35.0	313	32.0 ± 1.3	111
50 MM–Ni	37.2	172	31.3 ± 0.9	128

[a] Molecules CH_4 formed/site·sec.

20, 30, 40, and 50% mischmetal and the Harshaw 0302T catalyst. Once activated, a sample gave reproducible activities at any given temperature regardless of the direction of approach to the temperature. Activation energies obtained from these data were used to calculate a turnover number for each catalyst at 275°C. Turnover numbers (molecules CH_4 formed/site·sec) are shown in Table 1. For these calculations, the number of sites was assumed to be equal to the number of CO molecules chemisorbed by the sample after its activity had been measured.

Activated MM–Ni catalysts showed highest specific activity at the 30% MM composition where activity was over 10 times as great as No. 0302T—15% Ni on Al_2O_3. The catalyst containing 30% mischmetal also gave the highest total activity. Figure 2 shows the total conversion obtained with the MM–Ni catalysts at 210°C at a space velocity (SV) of 4000 hr^{-1}. Indications are that the optimum combination of specific activity and surface area development occurs at alloy compositions corresponding to the "$MMNi_5$" intermetallic (theoretically 32.3% MM). It should be emphasized that these activities are for steady state conditions when the catalysts were at equilibrium with the reaction mixture. The used Ni–Al–Al_2O_3 was shown by X-ray diffraction to contain Ni_3C as did the MM–Ni materials. As expected, the activity of supported nickel was found to be considerably less (after correction for pressure differences) than that reported by other workers for fresh nickel catalysts with clean surfaces (*6–9*). The MM–Ni catalysts are, on the other hand, comparable with clean nickel which indicates these materials are more resistant to the deactivation effects of carbon deposition and carbide formation.

Water formed during the methanation reaction was trapped out at room temperature to prevent plugging the gas control valve. Samples of the liquid were later analyzed by gas chromatography. This analysis showed the presence of small amounts of methanol and ethanol formed during the reaction. Because of the promising results obtained in this preliminary study, rare earth intermetallic compounds will be investigated further as catalysts for other hydrogenation reactions.

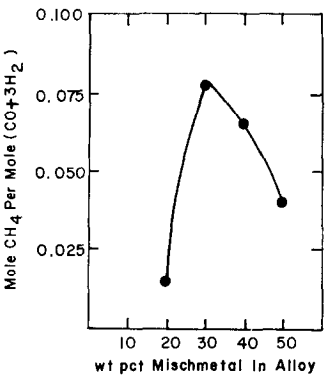

FIG. 2. Methane conversion for mischmetal–nickel alloys at 210°C, SV = 4000 hr^{-1}.

ACKNOWLEDGMENT

The authors thank Professor Paul Emmett for his invaluable advice and comments to the catalysis research group at the Reno Metallurgy Research Center.

REFERENCES

1. Sabatier, P., and Sendirens, J. B., *J. Chem. Soc.* **88**, 333 (1905).
2. Thomas, C. L., "Catalytic Processes and Proven Catalysts." Academic Press, New York, 1970.
3. Guidotti, R. A., Atkinson, G. B., and Wong, M. M., *J. Less-Common Metals*, **52-1**, 13 (1977).
4. Kuijpers, F. A., and Loopstra, B. D., *J. Phys. Suppl.* **32**, Cl-667 (1971).
5. Kuijpers, F. A., *Philips Res. Rept. Suppl.* 1973, No. 2.
6. Dalla Betta, R. A., Piken, A. G., and Shelef, M., *J. Catal.* **35**, 54 (1974).
7. Dalla Betta, R. A., Piken, A. G., and Shelef, M., *J. Catal.* **40**, 173 (1975).
8. Vannice, M. A., *J. Catal.* **37**, 449 (1975).
9. Vannice, M. A., *J. Catal.* **37**, 462 (1975).

GARY B. ATKINSON
LARRY J. NICKS

U. S. Bureau of Mines
Reno Metallurgy Research Center
Reno, Nevada 89512

Received April 29, 1976; revised December 16, 1976