Catalysis Letters 13 (1992) 323–329

Effect of the method of preparation of a Nd_2O_3–MgO catalyst on its efficiency in the reaction of oxidative coupling of methane

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Received 2 July 1991; accepted 11 March 1992

It is shown that the decomposition of a mixture of nitrates or coprecipitated carbonates or hydroxides of Mg and Nd form catalysts manifesting similar catalytic properties, while the catalyst obtained by impregnation is more active but much less selective. The mechanism of formation of the catalytically active phase and the nature of the active sites are discussed.

Keywords: Oxidative coupling of methane; effect of the catalyst; preparation method

1. Introduction

Oxides of rare earth elements (REE) exhibit high efficiency as catalysts for oxidative coupling of methane (OCM) [1,2]. The supporting of REE oxides on alkali earth oxides (MgO, CaO) permits the process to be carried out at high concentrations of the reagents and to obtain high concentration of the desired product (ethylene) [3,4]. Previous studies [5,6] demonstrate that low levels of REE dopant significantly affect the catalytic performance, an effect connected with the formation of active sites of oxidative character [5]. Additional information on the reaction mechanism and the formation of the active phase is, however, necessary for further improvement of these catalysts. The performance of 1 wt% Nd/MgO catalyst in OCM and the effect of the preparation method on the catalytic behaviour are described in the present paper.

2. Experimental

2.1. APPARATUS

The oxidation of methane was studied in a flow type quartz reactor with on-line gas-chromatographic analysis of the initial gas mixture and the products. A thermochrom 23 gas-chromatograph was used. The composition of the initial gas mixture and the flow rate were controlled by a Matheson four-channel electronic mass-flow controller.

0.060 g of the catalyst were usually charged in the reactor. The gas mixture methane : oxygen : argon = 15 : 5 : 80 was fed in at flow rate of 100 ml/min.

X-ray powder diffraction was carried out on a DRON-YM1 diffractometer, using Co K_α radiation.

2.2. ANALYTICAL

The reaction products were analysed gas-chromatographically in two columns: the first one containing Porapak Q for CO_2, C_2-hydrocarbons, and water separation, and the second one filled with 5A molecular sieve for hydrogen, oxygen, methane, and CO separation. The gas-chromatographic data were registered on a computing integrator based on a Pravetz 8C-computer. Additional processing of experimental data was effected using a Hewlett Packard 9845B desktop computer and a set of kinetic programmes [7].

2.3. CATALYSTS

Four different methods of preparation of catalysts containing 1 wt% Nd/MgO were studied. Sample N1 was prepared by impregnation of MgO with aqueous solution of neodymium nitrate. The support for this catalyst was obtained by decomposition of magnesium hydroxide at 873 K. Sample N2 was prepared by thermal decomposition of the dried residue of mixed magnesium–neodymium nitrate solution. Catalysts N3 and N4 were prepared by thermal decomposition of the mixed carbonate and hydroxide precipitated from the same solution with ammonium carbonate and hydroxide, respectively.

The thermal treatment of all four samples included drying at 393 K and calcination in air for 3 h at 1123 K. The specific surface areas for the catalysts N1, N2, N3, and N4, were 15.0, 2.5, 7.7, and 5.0 m^2/g, respectively.

3. Results

The experimental data (figs. 1–3) display the similar catalytic features for all four samples typical for a large number of oxide catalysts [8]: parallel formation

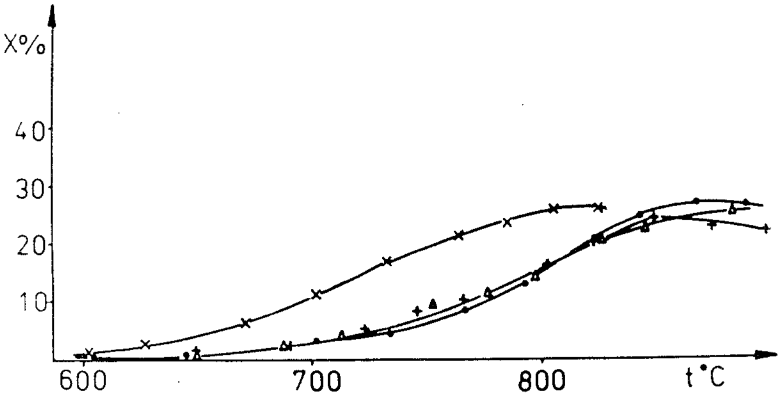

Fig. 1. The effect of the reaction temperature on methane conversion (X) for the investigated catalyst samples: N1 (×), N2 (△), N3 (○), and N4 (+).

of OCM products and products of complete oxidation, an increase of selectivity with the rise of temperature up to 1023 K, formation of ethane as the first product containing a C–C bond.

The reaction system reaches steady state under defined experimental conditions within about 5 min and the used catalysts display stable activity and selectivity. The N4 sample works with constant methane conversion and selectivity during 17 h on stream. Oxygen converts completely at temperatures above 1098 K for N1, 1123 K for N4, and 1148 K for N3. For the N2 sample, even at the highest temperature studied (1155 K), there is still about 3.5% oxygen in the reaction mixture. The oxygen depletion leads to leveling off the methane conversion at corresponding temperatures (fig. 1).

The catalytic activity of the Nd-doped catalysts is much higher compared to pure MgO (table 1). Comparison of the samples obtained by different methods

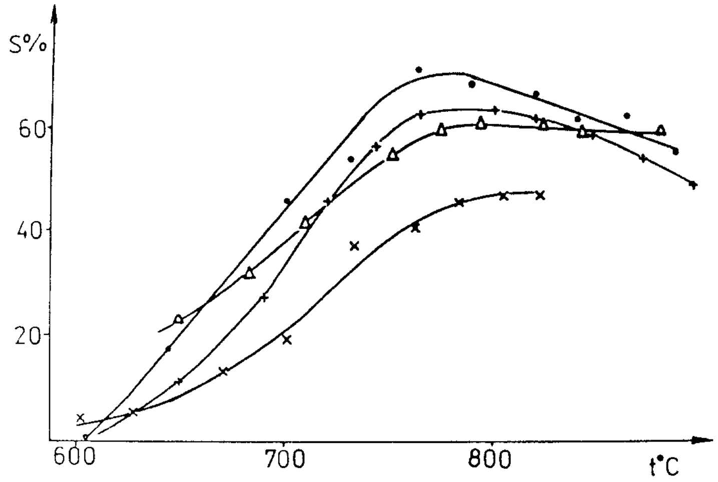

Fig. 2. The effect of the reaction temperature on C_2 selectivity (S) for the investigated catalyst samples: N1 (×), N2 (△), N3 (○), and N4 (+).

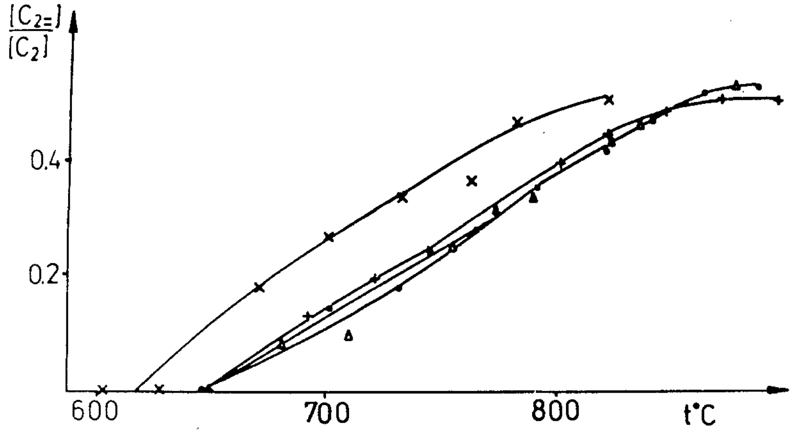

Fig. 3. The effect of the reaction temperature on the ethylene to C_2-hydrocarbons ratio ($[C_{2=}]/[C_2]$) for the investigated catalyst samples: N1 (×), N2 (△), N3 (○), and N4 (+).

shows that sample N1 is the most active. However, the selectivity of the samples N2–N4 at optimal reaction temperatures 1023–1123 K is substantially higher (fig. 2). Therefore, the maximum yield of OCM products on the sample N1 is 12% and on the samples N2–N4 up to 16%. The N2–N4 samples are also similar in the ratio of produced ethylene to C_2 products, while for N1 this ratio is higher (fig. 3).

The data obtained by X-ray diffraction (fig. 4) show the presence of two phases (MgO and Nd_2O_3) in the catalysts. The line width of the MgO phase increases with the increase of specific surface area reflecting the higher dispersity. The line width of the Nd_2O_3 phase in the impregnated sample is minimal, while for the sample N2 (prepared also from neodymium nitrate but using co-decomposition with magnesium nitrate) the lines are much wider.

Table 1
Specific rates of methane conversion (W) and ratios of the rates of methane transformation into C_2-hydrocarbons and total oxidation products (OCM/CO_x) at 1023 K

Catalyst	W ($\mu mol/min \cdot m^2$)	OCM/CO_x
MgO [a]	0.43	0.11
N1	14.35	0.32
N2	35.35	0.72
N3	16.05	0.85
N4	8.95	1.25

[a] MgO was obtained by magnesium hydroxide decomposition and calcination at 1123 K.

4. Discussion

High catalytic activity of the impregnated sample can be explained by its high specific surface area. The specific rate of methane conversion on this catalyst is on the intermediate position among the studied samples (table 1). But the ratio of the rate of C_2-hydrocarbons formation to the total oxidation rate is considerably lower on the sample N1. This fact reflects the influence of the preparation procedure on the concentration of the active sites on the surface.

The change in concentration of active sites may be a result of two different effects; (1) change of the surface morphology, (2) chemical modification of the surface or sub-surface layers.

The influence of the morphology on catalytic performance may be caused by the change of the concentration of dislocations or point defects on the surface, as well as the change of the content of the ions with low coordination number. The structural aspects for MgO catalysts prepared by different methods and used in OCM were studied in ref. [9]. It was demonstrated that the specific activity of the sample containing regular cubic crystallites was about 2.5 times higher compared to the material consisting mainly of agglomerates of small crystallites. This difference was caused mostly by the rates of deep oxidation, so the selectivity of more active catalyst was much less.

In the case of REE doped MgO catalysts obtained by impregnation, it was shown that both the rates of OCM and total oxidation increased with increasing doping level without significant change of the specific areas [5,6]. This effect was connected with the formation of the second phase of the REE oxide which was much more active and selective in OCM compared to MgO. For instance, the

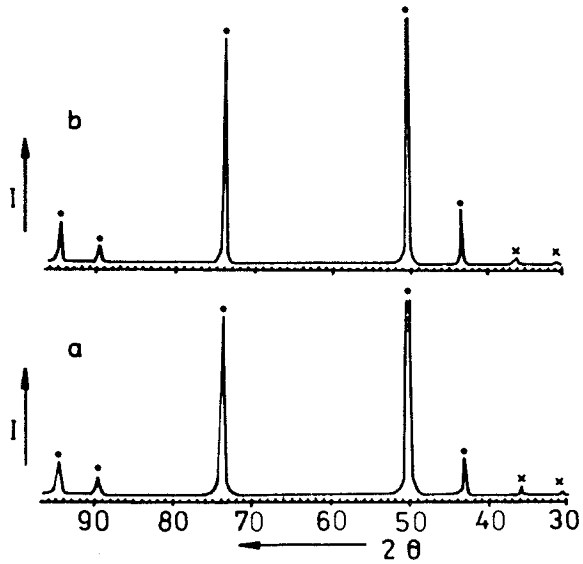

Fig. 4. XRD patterns of the N1 sample (a) and the N2 sample (b). (o) MgO, (×) Nd_2O_3.

data presented in table 1 show that sample N1 is more than 30 times more active compared to MgO and the ratio of the rates of OCM and total oxidation is increased three times by neodymium addition.

So, the high efficiency of the Nd/MgO catalysts is a result of the chemical modification. However, in the presence of the same amount of neodymium the catalysts obtained by different preparation methods display different catalytic performance in OCM. This effect may be caused by difference in the morphologies of the active phase. The data obtained by XRD show that the neodymium oxide phase in sample N2 is less regular compared to sample N1.

By transmission electron microscopy different morphologies of neodymium oxide in Nd/MgO catalysts were observed [10]: small clusters containing few Nd atoms, thin film on MgO surface, isolated crystallites on MgO surface and needle-like separated hexagonal crystals. Depending on the neodymium concentration and the preparation method the relative amounts of these forms of neodymium oxide were changed. As a rule, its structure in co-precipitated samples was less regular. This fact is in agreement with the data obtained in the present study. Therefore, it can be concluded that the precipitation of Nd_2O_3 precursor in the presence of considerable amounts of Mg^{2+} ions in the solution leads to the formation of rather irregular neodymium oxide.

The results obtained in ref. [10] and in the present study can be compared with our previous data obtained on impregnated Nd/MgO catalysts [5,6]. It was shown that the increase of Nd content in the sample led to Nd^{3+} EPR signal broadening. It means that the increase of doping level leads to the formation of neodymium oxide particles containing more Nd atoms. Linear correlation between the rate of C_2-hydrocarbons formation, neodymium content and the number of strong oxidizing sites able to oxidize molecular hydrogen in absence of oxygen in the gas phase was observed. It was suggested that the presence of oxidizing sites should be related to the substitution of Nd^{3+} ions by Mg^{2+} ions.

If both Nd^{3+} and Mg^{2+} ions are present in the solution during the formation of the precursor, a possibility exists for modification of the Nd_2O_3 phase by Mg^{2+} ions and stabilization of O^- ion-radicals in the form of $Mg^{2+}O^-$ pairs analogous to Li^+O^- pairs in Li/MgO catalysts [11]. These sites provide for the oxidative properties and activate methane via homolytic breaking of the C–H bond with the formation of methyl radicals [12–15].

However, when impregnating the MgO with nitrate solution, the presence of Mg^{2+} ions in the impregnation solution is caused by partial dissolution of the MgO surface (probably surface carbonate or hydroxide species) and therefore the number of Mg^{2+} ions in the solution and neodymium oxide phase is limited. If the preparation conditions provide for high concentration of magnesium ions in the initial solution, the formation of catalytically active substituted sites may be enhanced. It could be one of the causes for the formation of less regular neodymium oxide phase and the appearance of structure–activity correlations.

References

[1] K. Otsuka, K. Jinno and A. Morikawa, J. Catal. 100 (1986) 353.
[2] C.H. Lin, K.L. Campbell, J.X. Wang and J. Lunsford, J. Phys. Chem. 90 (1988) 534.
[3] V.R. Chouhary, S.T. Chaudhari, A.M. Rajput and V.H. Rane, J. Chem. Soc. Chem. Commun. 9 (1989) 555.
[4] Patent USSR, No. 1482905 (1987).
[5] M.Yu. Sinev, Yu.P. Tyulenin, V.Yu. Bychkov, B.V. Rozentuller and A.M. Rajput, *Proc IXth Soviet – Japanese Seminar on Catalysis Prepr.*, Yuzhno-Sakhalinsk, 1990, p. 75.
[6] M.Yu. Sinev, Yu.P. Tyulenin and B.V. Rozentuller, Kinet. Kataliz 32 (1991) 896.
[7] L. Petrov, A. Elias and D. Shopov, Appl. Catal. 18 (1985) 87.
[8] M.Yu. Sinev, V.N. Korchak and O.V. Krylov, Russ. Adv. Chem. 58 (1989) 38.
[9] J.S.J. Hargreaves, G.J. Hutchings and R.W. Joyner, Catal. Today 6 (1990) 481.
[10] M.Yu. Sinev, Yu.P. Tyulenin, G.J. Hutchings, R.W. Joyner, M.R.H. Siddiqui, C.J. Kiely and R.W. Devenish, *Proc. Symp. Natural Gas Upgrading*, ACS Meeting, San Francisco, April 6–9 1992.
[11] D.J. Driscoll, W. Martir, J.-X. Wang and J.H. Lunsford, J. Am. Chem. Soc. 107 (1985) 58.
[12] J.-X. Wang and J.H. Lunsford, J. Phys. Chem. 90 (1986) 5883.
[13] H.-S. Zhang, J.-X. Wang, D.J. Driscoll and J.H. Lunsford, J. Catal. 112 (1988) 366.
[14] C.-H. Lin, J.-X. Wang and J.H. Lunsford, J. Catal. 111 (1988) 302.
[15] X.D. Peng and P.C. Star, J. Catal. 128 (1991) 264.