Full paper/Mémoire

Structural study of the MO–Nd$_2$O$_3$ system obtained by a sol–gel procedure

Étude structurale du système MO–Nd$_2$O$_3$ obtenu par un procédé sol–gel

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A R T I C L E   I N F O

A B S T R A C T

The aim of the present work was to prepare a binary MO–Nd$_2$O$_3$ system by the sol–gel method and to characterise a series of mixed oxides belonging to the binary MO–Nd$_2$O$_3$ system (M = alkaline earth metal = Mg, Ca, Sr) to obtain suitable materials with catalytic properties. The molar ratio between the two oxides was MO/Nd$_2$O$_3$ = 95/5. Different precursors as alkaline earth metal oxide source (MO), various starting solution compositions expressed in various molar ratios between reactants and different synthesis parameters (pH, temperature and time of reaction) have been used. The structural study by X-ray diffraction analysis was accomplished based on the X-ray 5.0 program, which has established the presence of the mixtures of crystalline polyphases. The lattice constants, the average size of the crystallites, the average lattice strains and the mass of unit cell variation have been calculated. The program also allowed the calculus of the anisotropy factor, which can give the image of the structural disorder. The surface defects are a consequence of structural changes inside of the crystalline lattice of the solid solutions and are quite important for catalytic properties. Some catalytic activity measurements have established the potential of the prepared sol–gel mixed oxides to be used in the oxidative dehydrogenation process of light alkanes (C$_1$–C$_4$). Sample 3SrNd was shown to present the best catalytic activity and selectivity in olefins in propane conversion (C$_2^=$ & C$_3^=$) compared with 4Ca-Nd and 1Mg-Nd samples, which was interpreted as due to a better solid solution formation of Nd^{3+} in SrO, favoured by the close ionic radius of Sr^{2+} and Nd^{3+}, as well as by the high basicity of Sr and the presence of a greater number of point defects.

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R É S U M É

Le but de ce travail était de préparer par un procédé sol–gel et de caractériser une série d'oxydes mixtes appartenant au système binaire MO–Nd$_2$O$_3$ (métal M = alcalino-terreux = Mg, Ca, Sr) afin d'obtenir des matériaux ayant des propriétés catalytiques. Le

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rapport molaire entre les deux oxydes est : MO/Nd$_2$O$_3$ = 95/5. Différents précurseurs en tant que sources d'oxyde de métal alcalino-terreux (MO), diverses compositions de départ de la solution exprimées en différents rapports molaires entre les réactifs et différents paramètres de synthèse (pH, température, temps de réaction) ont été utilisés.

L'étude de la structure par analyse par diffraction des rayons X a été réalisée sur la base du programme X-ray 5.0, qui a établi la présence des mélanges de polyphases cristallines. Les constantes de réseau, la taille moyenne des cristallites, les contraintes de traction moyennes et la masse de la maille unitaire ont été calculées. Le programme a également permis le calcul du facteur d'anisotropie, qui peut donner l'image du désordre structural. Les défauts de surface sont une conséquence des changements structurels à l'intérieur du réseau cristallin des solutions solides et sont très importants pour les propriétés catalytiques. Des mesures d'activité catalytique ont établi le potentiel d'oxydes mixtes préparés par la méthode sol–gel pour être utilisés dans le procédé de déshydrogénation oxydante (ODH) d'alcanes légers (C$_1$–C$_4$). On a montré que les échantillons 3SrNd présentent les meilleures activités et sélectivités en oléfines dans la conversion du propane (C$_2^=$ & C$_3^=$) par comparaison avec les échantillons 4Ca–Nd et 1Mg–Nd. Cette propriété a été interprétée comme due à une meilleure formation de la solution solide de Nd^{3+} dans SrO, favorisée par des rayons ioniques proches de ceux de Sr^{2+} et Nd^{3+}, une basicité plus forte et la présence d'un plus grand nombre de défauts ponctuels.

1. Introduction

The light alkanes, C$_1$–C$_4$, are present in the natural gas and are also formed during the oil processing. One of the major objectives of the future chemistry consists in the finding of suitable active and selective catalysts for oxidative dehydrogenation (ODH) of the light alkanes into the highly valuable olefins such as ethylene, propene and butenes. At present, the most studied catalysts concern the ODH of ethane [1] and propane [2,3] and are different oxides of

- alkaline and alkaline earth (AE) elements: Li/X/MgO (X=Co, Sn, Cu Ti, Zr, Nb, Ce, B);
- transitional metals: V$_2$O$_5$, V$_2$O$_5$/SiO$_2$, V$_2$O$_5$/Al$_2$O$_3$, VMgO, V/α-Ti phosphate, MoVNbSb(Ca)O;
- rare-earth elements: La$_2$O$_3$, CeO$_2$, Sm$_2$O$_3$, Pr$_6$O$_{11}$ and so on;
- perovskite type: La$_{1-x}$Sr$_x$B$_{1-y}$M$_y$O$_{3-\delta}$ (B=Co, Cr, Fe, Cu, Mn, Y) (M = Nb, Ti); and
- supported noble metals: Pt/Al$_2$O$_3$.

From the literature data, it appears that the catalysts should contain redox elements to activate the alkanes and other elements to control the acid–base character of the surface for facilitating the fast desorption of the intermediate species.

In the 1980s, VMgO oxide was found to be rather active for ODH of propane. The basic character of the catalyst was suggested to favour the rapid desorption of the adsorbed olefin formed as intermediate from propane and, therefore, to avoid its further oxidation to oxygenates or CO$_x$. Unfortunately, the selectivity to propene was too low at high conversion to lead to commercialisation. The usual process of direct dehydrogenation of propane to propene on Pt-M/Al$_2$O$_3$ (M = Sn, Re, so on) or on chromium oxide–type catalysts remains the major industrial process at present, although it is quite endothermal and leads to coke formation and rapid deactivation of the catalyst, regenerated by burning off the coke to CO$_2$.

It clearly appears that the most active and selective metal mixed oxide catalysts in heterogeneous catalysis are in fact mixtures of several oxide phases. In this connection, a series of samples of mixed rare-earth oxides, as neodymium oxides, with alkaline earth oxides (AEOs) was studied to elucidate the complex relationship among the composition, catalyst structure and defects and the catalytic performance. The catalyst samples (5 mol % AEO) were prepared by the coprecipitation procedure from an aqueous solution of neodymium nitrate and an acidic solution (1 M oxalic acid) of the nitrate of AE element [4,5]. Doping of neodymium oxide with AEO improves its selectivity in the reaction of oxidative coupling of methane (OCM). Among them, strontium-doped Nd$_2$O$_3$ sample has the best selectivity towards higher hydrocarbons [4].

Burrows et al. [6] studied structure/function relationships in Nd$_2$O$_3$-doped MgO catalysts for the OCM reaction. Compared with pure MgO, the Nd$_2$O$_3$/MgO catalyst exhibits significant improvements in methane conversion efficiency and selectivity to C$_2$ hydrocarbons. The level of catalytic improvement was shown to be dependent on the Nd$_2$O$_3$ concentration and on the catalyst preparation method. The impregnation and coprecipitation routes (from nitrate, hydroxide and carbonate) have been used. The results strongly suggest that there is a certain neodymia morphology (or combination of morphologies) of the MgO, which is responsible for the increased catalytic activity and selectivity. The presence of a disordered and impure "glassy" neodymia phase is most effective in enhancing the OCM performance. The Nd$_2$O$_3$/MgO catalyst exhibiting the highest C$_2$ selectivity of 71.5% so far was the ex-carbonate coprecipitated sample.

The equimolecular mixture MO–Nd$_2$O$_3$ (M = Be, Mg, Ca, Sr) prepared starting from the tartrate complexes of the metals has been investigated in the OCM reaction [7]. The authors established a quantitative relationship between