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IMPACT OF THE CATALYST BASICITY ON THE MECHANISM OF OCM REACTION PERFORMED OVER ALKALINE EARTH –Nd_2O_3 MIXED OXIDES

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The oxidative coupling of methane (OCM) and the associate reaction mechanism for $C2^+$ formation over an equimolecular mixture of alkaline earth oxides (BeO, MgO, CaO and SrO) with Nd_2O_3 was investigated.
The equimolecular mixture of alkaline earth oxides with Nd_2O_3 catalyst was investigated by X-ray diffraction (XRD), temperature programmed desorption (TPD) and infrared spectra IR methods.
The concentration of surface basic sites contributing to the formation of C_2^+ was determined by measuring the amount of evolved CO_2 in the 300 – 820 ^oC temperature range. The turnover frequency (TOF) and the activation energy values were calculated by quantitatively determining the total number basic sites retaining CO_2.

INTRODUCTION

The basicity of oxide catalyst has been found to be a key factor in determining the activity for hydrocarbon generation. Since the basic sites have been suggested to play an essential role in OCM reaction, a closer look on their properties would be useful. The combination between alkaline earth oxides with lanthanide oxides proved to be efficient OCM catalysts. For example, the catalytic activity of cation (Mg^{2+}, Sr^{2+}, Ni^{2+}, $Mn^{3,\ 4+}$, Zr^{4+}) doped Nd_2O_3 was already investigated to some extent because of the interesting catalytic properties showed for OCM reaction.[1-3] The good catalytic performances of alkaline earth oxides have been attributed mostly to their strong alkaline sites.[4] Nd_2O_3 has been found also to contain medium and strong basic sites.[5] The effect of the insertion of the MgO, CaO, SrO, BaO into the host lattice of the Nd_2O_3 was investigated by Filkova *et al.*[6] The combination between the high basicity and good incorporation of strontium into Nd_2O_3 lattice was considered to be responsible for the good catalytic activity showed for OCM reaction The presence of strong strontium basic sites together with the incorporation into Nd_2O_3 lattice was considered to explain the high C_2^+ selectivity of the mixed oxides. In a recently published work, the catalytic behavior for oxidative conversion of methane in reducing conditions (oxidative coupling of methane) was investigated for the first time over pure and neodymium substituted zinc ferrites prepared by combustion method.[7]

The analyzing an eventual quantitative relationship existing between the basic properties of oxide materials and the active sites for methane activation are no published works.

The aim of this paper is catalytic behavior of equimolecular mixture of alkaline earth oxides (BeO, MgO, CaO and SrO) with Nd_2O_3 catalyst in OCM reaction and the quantitative relationship between the basic properties of these oxide materials and the active sites in coupling oxidative reaction of methane.

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EXPERIMENTAL

The type mixed oxides MO–Nd_2O_3 (M = Be, Mg, Ca, Sr) were prepared starting from the tartarate complexes of the metals. The complex precursors were synthesized by separately dissolving the metal nitrate and tartaric acid in minimum amounts of distilled water followed by the mixing of the resulted solutions. The molar ratio between M^{n+} and tartaric ion was in most cases one to four. The solutions containing the mixtures of complex metal tartarates were slowly heated and kept at 80 ^oC for 1 h. After cooling to room temperature, ethanol was added and then the pH was adjusted to 5.5–6 by using a solution of ammonium hydroxide in ethanol (1:1). The resulted light-yellow precipitates were maintained in liquid phase at 4 ^oC for 24 h, filtered, washed several times with ethanol and finally dried on P_4O_{10}. In all cases, the formation of insoluble heteropolynuclear complexes, having the general formula $(NH4)_x[MNd_2(Ta)_4(OH)_y]$ H_2O (M=Be, Mg, Ca, Sr), allowed an efficient mixing of component metal ions in the final oxide materials. The above-mentioned formulas were determined by elemental analysis. By using this preparation method, the washing out of component elements in preparation stage can be ruled out. The final step consisted in the air calcination of the precipitates at 800 ^oC for 2 h.

Activity tests for OCM reaction were performed at atmospheric pressure with 0.1 g of catalyst (0.3 - 0.8-mm fraction) loaded in a tubular quartz microreactor (i.d. = 8 mm). The reactant gaseous mixtures were prepared using electronic flow controllers (Aalborg). The typical total flow rates of the reaction mixtures where 24 cm^3/min STP (standard temperature and pressure) for OCM reaction. The corresponding GHSV (gas hourly space velocity) 14,400 h^{-1}. The composition of reaction mixtures were 41.6% CH_4, 8.4% O_2 (CH_4/O_2 = 5/1) in Ar. The O_2, CH_4 were separated and analyzed by using a molecular sieve 13X column whereas CO_2, C_2H_6 and C_2H_4 were determined on a Hayasept column (Buck Scientific - gas chromatograph).

The crystalline structure of the prepared samples was analyzed with a Rigaku Multiflex diffractometer provided with peak assignment software using Cu Kα radiation (λ = 1.54050 Å).

Temperature programmed desorption (TPD) experiments were carried out in a flow system, Ar carrier with 0.1 g of catalyst, by using a ChemBET 3000-Quantachrome Instruments type apparatus equipped with thermal conductivity detectors (TCD). The typical heating rate was 10^oC / min^{-1} and the total flow rate of the oxidizing or reducing gaseous mixtures was 70 ml min^{-1}. A mass spectrometer attached to the outlet confirmed that only CO_2 evolved from the sample. The IR spectra were recorded on KBr pellets with a JASCO FT-IR 4100 spectrophotometer in the 4000-400 cm^{-1} range.

RESULTS AND DISCUSSION

According to XRD data, presented in Fig. 1 the presence alkaline earth-oxides favored the formation of a well-crystallized hexagonal structure for Nd_2O_3. The hexagonal form of neodymia was found to perform better as OCM catalyst than the mixture of ordered cubic and hydrated phase of Nd_2O_3 [8]. The characteristic XRD lines of alkaline earth-oxides are either missing (MgO-Nd_2O_3) or are very weak (i. e. BeO-Nd_2O_3, CaO-Nd_2O_3 and SrO-Nd_2O_3).

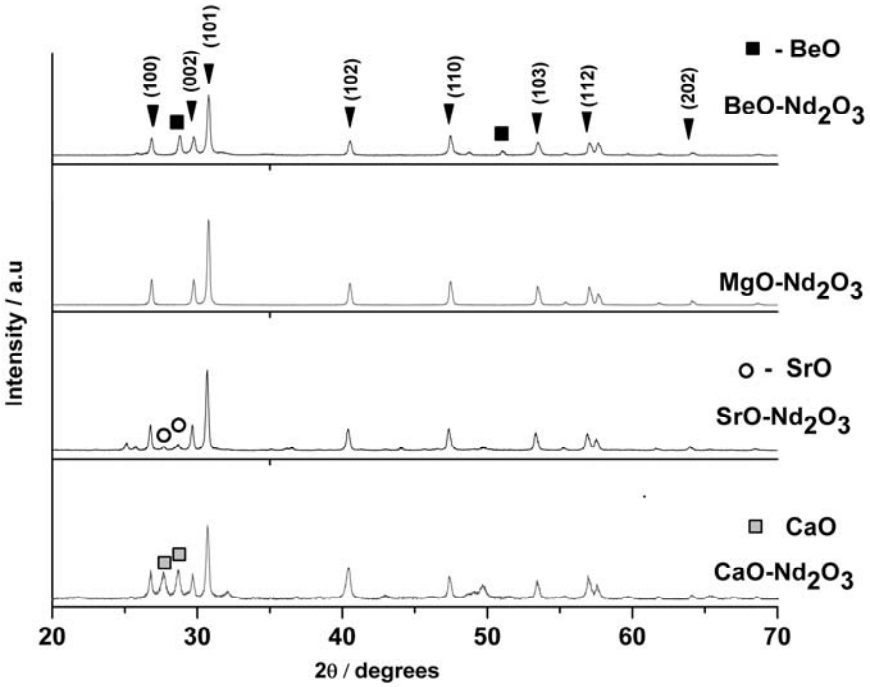

Fig. 1 – Comparative XRD spectra of MO-Nd_2O_4 (M= Be, Mg, Ca, Sr) compounds
▼- Nd_2O_3; ■ - BeO; ■ - CaO; ○ – SrO.

The yield of OCM reaction to C_2^+ *vs*. temperature over the investigated oxide mixture is presented in Table 1. In all cases, the $Y(C_2^+)$ showed a progressive increase with increasing the reaction temperature up to maxima at 775 ^oC. For T > 775 ^oC the reaction yield to C_2^+ hydrocarbons decreased, probably because of kinetic limitation. As can be seen in Table 1, the order of catalytic activity for hydrocarbon production at 775 ^oC was Ca > Mg > ≅ Sr > Be.

The selectivity to CO_2 (CO_2 levels as a function of reaction temperature) for the investigated oxide catalysts show a little dependency on reaction temperature. The formation of CO_2 takes place at the lowest OCM reaction temperatures by consuming most of the oxygen from reaction mixture, the concentration of CO_2 remaining afterward almost unchanged.

The comparative TPD profiles of spent mixed oxides are shown Fig. 2. The CO_2 desorption peaks observed in the case of BeO-Nd_2O_3 (at 528 and 639 ^oC) and MgO-Nd_2O_3 (at 606 and 668 ^oC) are consistent with different types CO_2 retained by the alkaline sites of mixed oxides. In the case of CaO-Nd_2O_3, only one large desorption peak could be observed at 678 ^oC. The TPD spectrum of SrO-Nd_2O_3 exhibits a low temperature CO_2 peak at 621 ^oC and a desorption peak located beyond highest temperature (820 ^oC) used in our measurements. The second observation is that the CO_2 desorption maxima are shifted to higher temperatures as the basicity of alkaline earth oxide increased from beryllium to strontium.[9]

The quantities of desorbed CO_2, calculated by integration of the surface area under TPD curves of Fig.2, are listed in Table 1. The total amount of desorbed CO_2 up to 820 ^oC, reflecting the basicity of the alkaline-earth oxides, increased from beryllium (0.24 mmol g^{-1}), magnesium (1.15 mmol g^{-1}) to calcium (2.2 mmol g^{-1}). The lower amount of desorbed CO_2 from SrO-Nd_2O_3 (1.33 mmol g^{-1}) compared to CaO-Nd_2O_3 can be explained by the higher stability of carbonate species on to the surface of strontium oxide. Thus, significant amount of carbonate remaining undecomposed on the surface at the end of TPD run.

Table 1

The catalytic performances (conversions, selectivity and yields to C_2^+) showed by alkaline-earths-Nd_2O_3 mixed oxides for OCM reaction at 775 ^oC

Catalysts	$X(CH_4)$/ %	$S(C_2+)$/ %	$Y(C_2+)_{max}$/ %
BeO-Nd_2O_3	21.28	40.71	8.66
MgO-Nd_2O_3	21.38	48.74	10.44
CaO-Nd_2O_3	23.08	51.97	11.78
SrO-Nd_2O_3	20.43	49.24	10.20

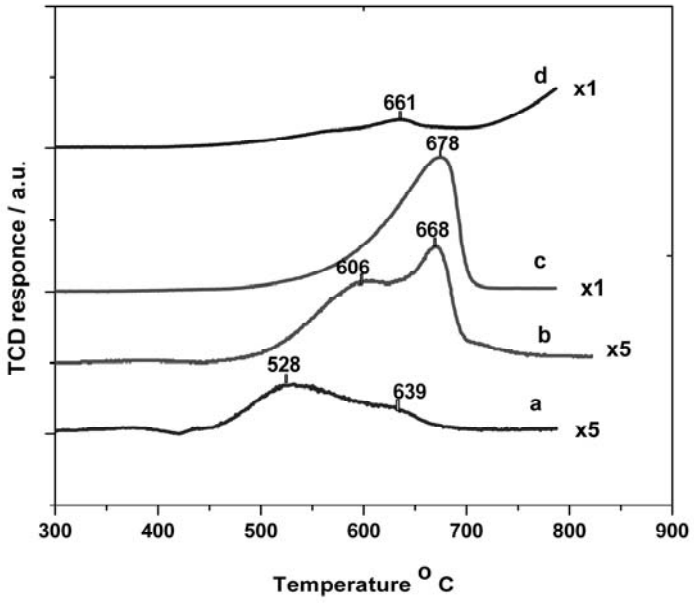

Fig. 2 – TPD spectra of CO_2 evolved from MO-Nd_2O_3 (M=Be, Mg, Ca, Sr) oxide catalysts used in OCM reaction, a-BeO-Nd_2O_3, b-MgO- Nd_2O_3, CaO- Nd_2O_3, d-SrO-Nd_2O_3.

Table 2

The amount of surface carbonate removed from the surface of mixed oxides up to 820 ^{o}C and the physical surface area (BET)

Catalysts	Amount of surface carbonate / mmol CO_2 g^{-1}	S_{BET} / m^2 g^{-1}
$BeO-Nd_2O_3$	0.24	7.1
$MgO-Nd_2O_3$	1.15	6.5
$CaO-Nd_2O_3$	2.2	6.0
$SrO-Nd_2O_3$	1.33	6.4

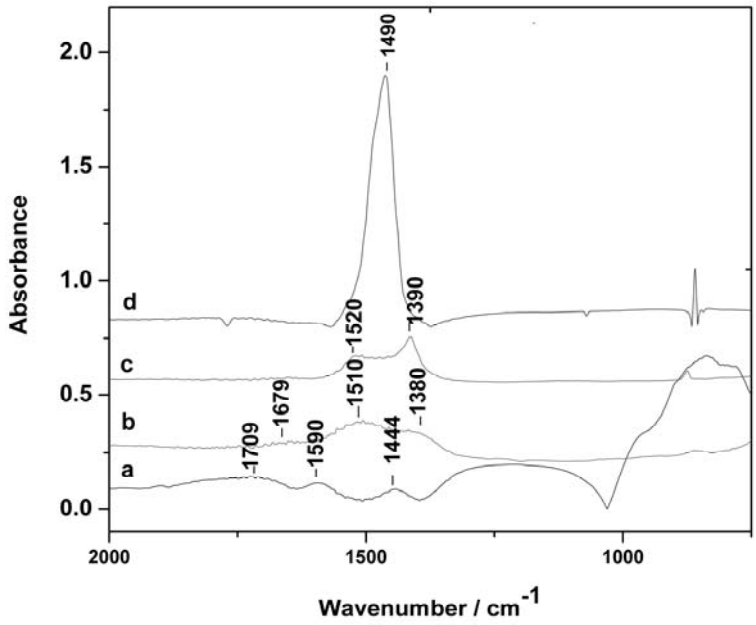

Fig. 3 – Comparative IR spectra of the MO–Nd_2O_3 oxides (M = Be, Mg, Ca and Sr).
a- BeO-Nd_2O_3, b-MgO- Nd_2O_3, c-CaO- Nd_2O_3, d-SrO- Nd_2O_3.

Table 3

Comparative IR results of the MO-Nd_2O_3 oxides (M= Be, Mg, Ca and Sr)

	Carbonate species	**Wave number /cm^{-1}**
$BeNd_2O4$	bidentate	1709
	unidentate	1590, 1444
$MgNd_2O4$	unidentate	1510,1380
	bidentate	1679,
$CaNd_2O_4$	unidentate	1520,1390
	bidentate	1645
$SrNd_2O_4$	monodentate and bidentate	1490 (broad peak)

The IR results confirmed the presence of carbonate species on the investigated oxide materials. The surface carbonate species formed on the surface of MO-Nd_2O_3 mixed oxides were investigated by IR spectroscopy. Fig. 3 presents the IR spectra of the mixed oxides used in OCM reaction.

Table 3 presents the IR results of the mixed oxides used in OCM reaction. IR bands characteristic for different surface carbonate species could be identified in the 1380 – 1708 cm^{-1} region for all the investigated oxides.

Thus, the peak at 1709 can be assigned to CO_2 adsorbed on Nd_2O_3 [10] whereas the other two peaks can be attributed to the carbonate species located on the alkaline sites of MO. In the case of MO-Nd_2O_3, (M= Be, Mg, Ca) three characteristic IR band have been observed around of values 1400, 1500 and 1700 cm^{-1}. Thus, it can be assumed that the surface carbonate species are more or less

related to the alkalinity of MO. On simple MO, the characteristic IR bands at 1500 and 1400 cm^{-1} are characteristic to unidentate CO_2 whereas the bidentate carbonate species are characterized by an IR band at 1670 cm^{-1} [11] $SrO\text{-}Nd_2O_3$ sample shows only one broad IR band with the maxima located at 1490 cm^{-1}. The main IR bands of carbonate species on SrF_2/Nd_2O_3 surface were detected at 1420 and 1520 cm^{-1}. [12] From the surface area of the IR peak attributable to carbonate species, it can be said that the largest amount of carbonate is formed on $SrO\text{-}Nd_2O_3$. It is also clear that the broad IR band at 1490 cm^{-1} contains the characteristic vibration of both, monodentate and bidentate carbonates.

According to IR results, (i) monodentate as well as bidentate carbonate species is formed on the surface of all mixed oxides, (ii) the alkaline earth oxides are mostly responsible for the formation of surface carbonate species and (iii) the amount of surface carbonate correlates well with the basicity of the alkaline earth oxide, increasing from BeO to SrO.

The concentration of surface basic sites contributing to the formation of C_2^+ was determined by quantitatively measuring the amount of desorbed CO_2 in the 300 – 820 ^oC temperature range. The amount of surface basicity correlates well with the catalytic activity for C_2^+ production (at 775 ^oC) for all the investigated mixed oxides. The material showing the higher basicity ($CaO\text{-}Nd_2O_3$) in term of capacity of retaining removable CO_2 showed the best performances for C_2^+ production. It should be emphasized that the surface carbonate originates from the history of material preparation (tartarates are used as oxide precursors) as well as from the CO_2 resulted from the unselective oxidation of CH_4.

The formation of C_2^+ starts at the moment when the basic sites become available as a result of CO_2 desorption. According to TPD results in fig. 2, the desorption of CO_2 starts at T>500 ^oC. This correlates well with the beginning of C_2^+ formation at T≥525 ^oC.

Table 4

The rate of C_2^+ formation over $MO\text{-}Nd_2O_3$ mixed oxides (M=Be, Mg, Ca, Sr), the associated TOF at 775 ^oC and the activation energy values

Catalysts	**Rate of C_2^+ formation /mol $s^{-1}g_{cat}^{-1}$**	**TOF (C_2^+) /s^{-1}**	**Ea /Kcal/mol**	
			a	**b**
$BeO\text{-}Nd_2O_3$	1.82×10^{-6}	0.126	8.4	5
$MgO\text{-}Nd_2O_3$	2.60×10^{-6}	0.037	11.2	14.3
$CaO\text{-}Nd_2O_3$	2.37×10^{-6}	0.017	15	17
$SrO\text{-}Nd_2O_3$	2.24×10^{-6}	0.028	2	9.2

[a] The activation energies calculated from the slopes of the ln(TOF(C2+) *vs* 1/T plots
[b] The apparent activation energies calculated from slopes of the ln(rate of C2+) *vs* 1/T plotes

The reaction rates as well as the TOF (turnover frequency) values for C_2^+ formation at 775 ^oC over the investigated mixed oxides are presented in Table 3. The TOF values were calculated by dividing the experimentally measured reaction rates (see Table 3) to number of basic sites responsible for C_2^+ formation. It should be emphasized that this is the first attempt ever made to estimate the TOF values of C_2^+ formation over oxide catalysts. Studies reporting on the determination of hydrocarbon oxidation TOF on metal oxides are very scarce. The main difficulties consisted in the identification of active sites and in finding reliable experimental methods for measuring their concentration. The TOF values for methane partial oxidation over Ru supported on $Ta_2O_5\text{-}ZrO_2$ and $Nb_2O_5\text{-}ZrO_2$ at 500 ^oC ranged between 2.1 and 2.8 s^{-1}. [13] In this case, the catalytic active sites have been determined by CO chemisorptions.

The variation of TOF values with the nature of alkaline-earths combined with Nd_2O_3 is presented in Table 4. The TOF minimum was observed for $CaO\text{-}Nd_2O_3$ and the highest one was determined for $BeO\text{-}Nd_2O_3$. High concentration of alkaline sites (i. e. the case of $CaO\text{-}Nd_2O_3$) gave lower TOF for C_2^+ formation. The synergetic effect between the alkaline earth oxides and Nd_2O_3 may be also an important factor mediating a complex relationship between concentration, strength of alkaline active and TOF for C_2^+ production.

The activation energies were determinate from the slopes of the of the logarithmic plots of TOF or rate of C_2^+ formation *vs.* 1/T.

Comparative values of the activation energies and apparent activation energies of mixed oxide are presented in Table 4. The values of apparent activation energies obtained from the rate of C_2^+ formation are greater that values of obtained from TOF date. The order of values of activation energies for C_2^+ formation is BeO-Nd_2O_3< MgO-Nd_2O_3<CaO-Nd_2O_3 <SrO-Nd_2O_3. This values presented in the table 4 is in a relative good agreement with the date reported in literature.[14, 15]

CONCLUSIONS

Our experimental results support also the idea that methane is converted to products on two types of active sites by independent pathways. The alkaline active sites (A) responsible for C_2^+ formation are inactive at low temperature because they are blocked by CO_2. By raising the reaction temperatures these sites start to be progressively available for methane activation because of CO_2 desorption. The concentration of available active sites at a given reaction temperature is dependent on the thermal stability of surface carbonate. The formation of CO_2 product takes place on B type sites showing no interaction with CO_2. Thus the production of CO_2, starting at low temperatures, is relatively independent on reaction temperature.

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