Surface Interaction between Methane and Alkali/Alkaline-Earth Oxide Catalysts

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The interaction of methane with alkali/alkaline-earth oxide catalysts (NaOH–CaO, NaOH–BaO–CaO) was investigated at 350, 500 and 750°C using X-ray photoelectron spectroscopy. Methane interacted with surface carbonate at temperatures of 500 and 750°C while no reaction was observed at 350°C. Intermediate states registered on the surface consisted of methoxy species and carbonyl groups. Mechanistic aspects of the high-temperature oxidative methane conversion reaction tentatively derived from these results are discussed. © 1991 Academic Press, Inc.

INTRODUCTION

It is generally assumed that the mechanism of the oxidative coupling reaction of methane consists of several steps occuring in parallel and in series (*1–4*) comprising the following reactions:

(a) formation of methyl species on the catalytic surface,

(b) gas-phase and/or surface recombination of methyl radicals to form ethane,

(c) oxidative and/or thermal dehydrogenation of ethane to ethylene, and

(d) nonselective oxidation of radicals and various C_2 species to CO and CO_2.

Catalytic oxidative methane coupling to ethane and ethylene has been extensively studied using alkali/alkaline-earth compounds as catalysts (*4–12*). There is, however, rather little information on the elementary reaction steps to CO_x for this type of catalyst. For Sm_2O_3, La_2O_3, or Li–MgO catalysts (*13*) it has been suggested that CO_2 is formed from C_2 hydrocarbons on the same active sites as those where the methyl radi-

cals leading to C_2 formation are produced. Iwamatsu and Aika (*12*) derived from kinetic studies that both C_2 hydrocarbons and CO_x originate on $NaNO_3$–CaO and $LiNO_3$–CaO catalysts from the same intermediate; i.e., the methyl species oxidized by active surface oxygen is transformed to a methyl-peroxy radical. An advanced understanding of these nonselective oxidation processes would certainly assist in the design of more selective catalysts. In the present contribution the interaction of methane with surfaces of alkali/alkaline-earth oxide catalysts was studied. Sodium hydroxide–calcium oxide and sodium hydroxide–barium–calcium oxide catalysts were exposed to methane at temperatures ranging from 350° to 750°C and the surface composition of the unexposed catalysts and those exposed to methane was studied using X-ray photoelectron spectroscopy with special attention to carbon-containing species on the surface and to the changes in sodium, barium, and calcium cation content upon methane exposure.

EXPERIMENTAL

Catalysts

In order to elucidate the change in catalyst surface composition and the formation and/

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or change of carbon-containing species upon exposure to methane, sodium and calcium or sodium, barium, and calcium containing catalysts were studied. The catalysts were prepared by the incipient wetness method in the following way:

NaOH–CaO: $Ca(OH)_2$ was impregnated with an aqueous solution containing 2 mol% NaOH; then the solid material was dried at 120°C and subsequently calcined in nitrogen at 750°C (catalyst C-1).

NaOH–BaO–CaO: $Ca(OH)_2$ was impregnated with an aqueous solution containing 1 mol% of NaOH; this precursor was subsequently dried at 120°C before an additional impregnation was carried out using an aqueous solution of 10 mol% of $Ba(CH_3COO)_2$. After further drying at 120°C the catalyst precursor was calcined in synthetic air at 600°C (catalyst C-2).

Experimental Procedures

Both types of catalyst were calcined in a quartz reactor from which they were quickly moved to the preparation chamber of the XPS spectrometer (Leybold AG LH-10). The experimental procedure consisted in all cases of the following stages:

(a) unless stated otherwise, pretreatment in vacuum at the desired temperature for 1 hr, followed by cooling, taking the XPS spectrum, and repeated heating according to the temperature program specified below;

(b) addition of methane at 1 bar and room temperature followed by raising the temperature to the desired value and further exposure to methane for the specified period;

(c) removal of methane at the reaction temperature (unless stated otherwise);

(d) taking the XPS spectrum;

(e) in specified cases, repeating b–d at the same or changed temperatures as described below.

Four types of experiments (no. 1 to 4), each starting with a new calcined sample, were carried out:

Experiment no. 1: Catalyst C-1 was inves-tigated. The temperature program applied in the pretreatment procedure consisted of heating at 640, 670, 700, 730, and 760°C. Exposure to methane followed at 750°C for 10 min.

Experiment no. 2: Catalyst C-1 was investigated without vacuum pretreatment. The catalyst was exposed to methane at 750°C for 10 min.

Experiment no. 3: Catalyst C-1 was investigated according to the procedure described in b–e without vacuum pretreatment. The temperatures and periods of exposure to methane were 350°C for 10 min, 350°C for an additional 30 min, 500°C for 10 min. The experiment was completed by heating the sample in vacuum at 500°C for 30 min and taking the XPS spectrum.

Experiment no. 4: Catalyst C-2 was investigated according to the procedure b–e, without vacuum pretreatment. The catalyst was exposed to methane at 750°C for 10 min and then additionally twice for 30 min, i.e., 10,40, or 70 min. After each exposure to methane, methane was removed with simultaneous cooling of the sample.

EVALUATION OF XPS SPECTRA

For evaluating the XPS spectra Na $1s$, Ba $3d_{5/2}$, Ca $2p$, O $1s$, and C $1s$ peaks were used to calculate the surface composition of the elements using Wagner's sensitivity factors (14). Sodium, barium, and oxygen (O $1s$, oxide) peaks were calibrated for charge shift using the Ca $2p_{3/2}$ peak while the peaks for carbon and oxygen (O $1s$, OH /CO_3^{2-}), and for reasons of better identification in some instances also the sodium peak, were calibrated to the C $1s$ (adventitious carbon) peak at 284.7 eV in the case of methane treated samples. Calibration for charge shift for the calcined sample was done using the Ca $2p_{3/2}$ peak. Only for methane-treated samples was differential charging observed, which suggests that the heterogeneity of the catalyst increases. It is assumed that heterogenous "patches" of differently charged sodium compounds and/or carbon species are formed on the surface of the catalyst.

Sodium, which is strongly enriched on the surface (see below), may partly belong to this form, which is different from that of the bulk of the catalyst. When calibrated against C $1s$ the position of the Na $1s$ peak is 1071.5 eV, which corresponds to Na_2CO_3. Therefore, it may be assumed that the observed peak is a superposition of the peaks of sodium species (NaOH, Na_2CO_3) belonging to two differently charged forms.

RESULTS AND DISCUSSION

The interaction of NaOH–CaO or NaOH–BaO–CaO catalysts with methane influences the chemical state and composition of the components on the catalyst surface, depending on the temperatures of methane exposure and its subsequent removal. The chemical state and composition of metal cations, oxygen, and carbon on the surface are discussed in the following paragraphs. Special attention is paid to the reaction of carbon-containing species on the surface during the reaction with methane.

(1) Chemical State of Components on the Surface

Binding energies of sodium, barium, calcium, oxygen, and carbon for C-2 catalyst calcined at 600°C and then heated in methane at 750°C are given in Table 1 from which the following can be derived.

(a) Sodium exists on the surface as a mixture of its oxide, hydroxide, and carbonate after calcination. Carbonate formation may have been caused by the handling of the calcined sample. The position of the Na $1s$ peak measured after exposure to methane is, for reasons already stated, inconclusive.

(b) As is to be expected, neither sodium nor barium or calcium is reduced during exposure to methane.

(c) Oxygen exists as OH^- and/or CO_3^{2-} as well as oxide. After the reaction with methane the two oxygen peaks show different behavior; oxygen in OH^- or CO_3^{2-} groups seems to be shifted in a similar way to the carbon peak, which would imply that this oxygen peak belongs to the uppermost layer together with carbon.

(d) There are two C $1s$ peaks for the calcined sample; the first is related to adventitious carbon and the other one to carbonate. After the exposure of the solid sample to methane an additional C $1s$ peak appears at ca 287.6 eV for sample A (10 min-heated catalyst) and 286.6 eV for samples B and C

TABLE 1

Binding Energies of Sodium, Barium, Calcium, Oxygen, and Carbon for a NaOH(1 mol%)–Ba(CH$_3$COO)$_2$ (10 mol%)–Ca(OH)$_2$ Catalyst (C − 2) Calcined at 600°C and then Heated in Methane at 750°C for Different Periods of Time

Sample	Na $1s$	Ba $3d_{5/2}$	Ca $2p_{3/2}$	O $1s$	O $1s$	C $1s$		
					OH/CO_3^{2-}	Adventitious carbon	$-\overset{\shortmid}{\underset{\shortmid}{C}}-O-$ or $>C=O$	CO_3^{2-}
calcined	1072.1	780.6	346.5	529.0	531.5	285.0	—	289.9
A[a]	1072.7	781.1	346.5	529.5	531.2*	284.7*	287.6*	289.7*
B[b]	1072.6	781.2	346.5	529.5	531.1*	284.7*	286.4*	289.3*
C[c]	1072.8	781.2	346.5	529.7	531.3*	284.7*	286.6*	289.6*

Note. All binding energies were calibrated either to Ca $2p_{3/2}$ (346.5 eV) or to C $1s$ (284.7 eV); the C $1s$ calibration is indicated by an asterisk (*).

[a] Heated for 10 min.
[b] Heated for 40 min.
[c] Heated for 70 min.

TABLE 2

Content of Sodium (Na + Ca = 100 at.%) on the Surface of (NaOH(2 mol%)–CaO) Catalyst C-1 After Different Pretreatments

Experiment		Pretreatment					
		Vacuum				CH₄	
No. 1	None 1h 28.1	640°C 1h 21.1	670°C 1h 19.5	700°C 1h 22.3	730°C 1h 21.7	760°C 1h 22.9	750°C 10 min 45.4
No. 2	None 36.3	CH₄ 750°C 10 min 46.8					
No. 3	None 32.1	CH₄ 350°C 10 min 22.4	CH₄ 350°C 40 min 24.0	CH₄ 500°C 10 min 30.2	vacuum 500°C 30 min 31.1		

(40 and 70 min-heated catalysts). The 287.6 eV peak may be ascribed to aldehydes or ketones since the binding energy is characteristic for the $\diagdown C = O$ group (14); the 286.6 eV peak is, however, due to $-\overset{|}{C}-O-$ groups (i.e., alcohol, ester, ether, peroxide) (15). The binding energies of sodium, calcium, and oxygen for the C-1 catalyst show the same pattern for both the C-1 and C-2 catalysts. There is, however, only one C $1s$ peak in all cases at ca 289.5 eV corresponding to CO_3^{2-} groups. It may therefore be assumed that during the reaction of carbonate with methane, lower-oxidation-state products are formed as unstable intermediates.

The amount of sodium on the surface strongly increases on heating in methane for both experiments carried out at 500 and 750°C but it slightly decreases for the catalyst heated in vacuum at 350°C in methane or at 640–760°C in vacuum. Since sodium was also found on the sample holder it is implied that the sodium compound melted and spread over the system. It does not appear justified to assume that sodium compounds evaporated from the samples and solidified afterwards on the holder because the sample holder was heated to the same temperature as the sample. As the melting points of NaOH and Na₂CO₃ are 318.4 and 851°C, respectively, it may be assumed that

(2) Changes in the Surface Composition of the Catalyst upon Heating in Methane

The surface-cation content of samples C-1 and C-2 before and after exposure to methane is given in Tables 2 and 3 and described below. (To illustrate the changes in the content of alkaline earth metal cations on the surface more clearly, only concentrations of the metal cations, i.e., Na and Ca or Na, Ba, and Ca, are considered and set equal to 100%.)

TABLE 3

Surface Composition of the NaOH–BaO–CaO Catalyst Calcined at 600°C and Subsequently Exposed to Methane at 750°C

Sample	Time of exposure (min)	Composition (at.%)		
		Na	Ba	Ca
calcined	—	17.2	6.8	76.0
A	10	33.6	8.7	57.7
B	40	50.7	9.2	40.1
C	70	55.5	10.2	34.4

sodium carbonate was reduced by methane at 500 or 750°C to form sodium hydroxide and lower-oxidation-state carbon species, as is discussed later. It seems justified to exclude evaporation of NaOH, as the boiling point of this compound is 1390°C and its vapor pressure is low (1.3 mbar at 739°C). On the other hand, as shown later, there was no change in the amount of carbonate and therefore no carbonate reduction while heating at 350°C in methane or at temperatures ranging from 640 to 760°C in vacuum. Changes in the amount of barium were only slight after heating in methane. The calcium content decreased with increasing exposure time significantly according to the increase in sodium.

(3) Reaction of Carbon-Containing Species on the Surface during Exposure to Methane

In order to elucidate the formation of carbon-containing species on the catalytic surface upon reaction with methane, the surface composition for C-1 and C-2 was determined. The results for the C-1 catalyst, omitting the oxygen content as being irrelevant for the following discussion, are listed in Tables 4a–4c and explained below.

The amount of surface carbonate does not change within experimental accuracy upon

TABLE 4b

Surface Composition of Catalyst C-1 (NaOH (2 mol%)–CaO) Calcined and Exposed to Methane (Na + Ca + C = 100 at%; C as CO_3^{2-})

Treatment	Composition (at.%)		
	Na	Ca	C as CO_3^{2-}
calcined outside XPS equipment at 750°C in N_2	23.5	41.3	35.2
heated in CH_4, 750°C, 10 min	40.5	46.1	13.4

heating in vacuum at temperature between 640 and 760°C or in methane at 350°C even for prolonged times of 10 to 40 min. This would suggest that there is neither carbonate decomposition on heating (640 to 760°C) in vacuum nor any reaction of methane with the surface carbonate at 350°C. To support this view, it should be mentioned that a similar tendency was observed for TiO_2: adsorbed surface formate desorbed readily from this solid sample for T < 400°C, but once carbonate was formed it could only be removed by heating in oxygen (16). However, heating in methane at 500 or 750°C (experiments 1, 2, and 4) results in a drastic decrease in the amount of carbonate on the surface, which means that methane reacts with surface carbonate. Heating the reacted

TABLE 4a

Surface Composition of Catalyst C-1 (NaOH (2 mol%)/CaO) Calcined, Heated at Different Temperatures in Vacuum, and Exposed to Methane (Na + Ca + C = 100 at%; C as CO_3^{2-})

Treatment	Composition (at.%)		
	Na	Ca	C(CO_3^{2-})
calcined in external equipment at 750°C in N_2	21.4	54.8	23.8
heating in vacuum, for 1 h			
640°C	16.2	60.6	23.2
670°C	15.1	62.4	22.6
700°C	17.4	60.6	22.0
730°C	17.2	62.0	20.8
760°C	18.3	61.6	20.1
heating in 1 bar of CH_4 at 750°C for 10 min	42.3	50.8	6.9

TABLE 4c

Surface Composition of Catalyst C-1 (NaOH (2 mol%)–CaO) Calcined and Exposed to Methane at 350 or 500°C or Heated in Vacuum (Na + Ca + C = 100 at%; C as CO_3^{2-})

Treatment	Composition (at.%)		
	Na	Ca	C(CO_3^{2-})
Calcined outside XPS equipment in N_2 at 750°C	23.0	48.6	28.4
Heated in CH_4 at 350°C for 10 min	17.5	60.5	22.0
Heated in CH_4 at 350°C for 40 min	18.2	57.7	24.2
Heated in CH_4 at 500°C for 10 min	27.7	64.0	8.3
Heated in vacuum at 500°C for 30 min	28.1	62.2	9.7

TABLE 5

Surface Composition of Catalyst C-2 (NaOH–BaO–CaO) Calcined and Subsequently Heated in Methane at 750°C

Sample	Time of exposure (min)	Composition (at %)					
		O	Na	Ba	Ca	C(CO_3^{2-})	C($\searrow$C$=$O or $-\overset{\mid}{\underset{\mid}{C}}-O-$)
calcined	—	73.7	3.2	1.3	14.4	7.4	0
A	10	59.0	9.7	2.5	16.6	8.9	3.3
B	40	59.5	15.1	2.7	11.9	6.3	4.4
C	70	61.2	15.0	2.8	9.3	4.5	7.2

Note. Na + Ba + Ca + O + C = 100%; C as CO_3^{2-}, $\searrow$C$=$O, or $-$C$-$O$-$.

sample in vacuum at 500°C does not lead to any further change in the XPS spectrum, suggesting that no carbonate decomposition occurs in the absence of methane. As mentioned before, intermediate products in the reaction of carbonate with methane were observed for catalyst C-2. Table 5, which gives the total composition as Na + Ba + Ca + O + C = 100% (C: CO_3^{2-} or $\searrow$C$=$O or $-\overset{\mid}{C}-$O$-$), illustrates the process of formation of the suggested intermediates. The total amount of carbon grew in experiment no. 4 for A (10 min of exposure) and remained afterwards stable for B and C (40 and 70 min of exposure to methane, respectively). The proportion of carbonate grew slightly for A; for prolonged exposure time the amount of carbonate decreased while the contribution of the $\searrow$C$=$O or $-$C$-$O$-$ groups increased; the higher the exposure time, the lower the proportion of carbonate in the total surface carbon. The total amount of carbon as CO_3^{2-}, $\searrow$C$=$O, or $-$C$-$O$-$ groups remained stable, however. The oxygen content decreased after 10 min of exposure to methane and remained fairly stable after extended periods of exposure times.

From the above results the following may be derived:

(a) There is a reaction of methane with surface carbonate species in the high-temperature region (500°C, 750°C) but no reaction in the low-temperature region (350°C).

(b) As intermediate species formed from carbonate could only be detected if the sample was cooled at the same time as methane was removed and no intermediate species were found when the sample was outgassed at the temperature of exposure to methane, it may be assumed that intermediate species are unstable both at 500 and 750°C. This is in agreement with studies for oxides using thermal decomposition, isotope tracer, and infrared experiments which showed that surface methoxy species did not persist above 250°C to ca. 500°C (*17–20*). The species observed in experiment 4 could not, however, be formed at a lower temperature because no surface reaction of carbonate with methane took place at 350°C (experiment 3). On the other hand, adsorption of total oxidation products from the gas phase may be excluded because there is no oxygen in the gas phase to form CO and CO_2. Even if some very small amounts of carbon oxide had formed from methane by some kind of oxidizing species desorbed from the surface (oxygen or water), CO adsorption on CaO at low temperatures was found by IR and UV spectroscopies not to lead to ketonic structures but metallated formate (*21, 22*) or "carbonite" ion CO_2^{2-} (*23*) species as an intermediate. In the presence of oxygen these intermediate species form carbonate (*21–24*). Similarly, reaction of CO with MgO or Al_2O_3 resulted in the development of surface formates (*25*) in the temperature range from 102 to 297°C. Adsorption of formaldehyde on TiO_2 at temperatures lower than 400°C also gave rise to surface formate, as shown by infrared spectroscopy (*26*).

Although the investigated reaction of carbonate with methane is a reduction process in the absence of oxygen, conclusions concerning the total oxidation of methane may be drawn if this process is considered to be the reversible one of the reductive reaction of methane with carbonate. It may be postulated that high-temperature oxidation includes a surface reaction of methane with oxygen with formation of unstable intermediates containing methoxy species and ke-

tonic groups. Similarly, a surface-located oxidation accompanying a gas-phase CO_x formation was postulated by Lo *et al.* (*27*) when using potassium-doped Sb_2O_4–SiO_2 catalysts. The surface-assisted CO_x formation is believed to involve either methyl radicals or direct interaction of methane with surface oxygen species leading to CO_2 probably via methyl-peroxide radicals as suggested by Ito *et al.* (*5*). An adsorbed radical of this type certainly cannot be excluded as an intermediate since one of the unstable intermediates observed in this study contains the $-\overset{|}{C}-O-$ group but the experimental data are also consistent with the assumption of the methoxy radical as outlined above.

The above reasoning does not exclude selective C_2 formation by methane coupling in the absence of oxygen, which was observed by Schäfer (*28*) in pulse experiments using 11% NaOH-on-CaO catalyst. Due to the design of the present experiment no C_2 hydrocarbons were looked for. Our findings are in agreement with work of Mirodatos *et al.* (*29*), who found that initial contact of methane and oxygen resulted in the irreversible adsorption of methane and/or reaction products held on the surface most probably as total oxidation products, i.e., carbonates.

CONCLUSIONS

In the presence of alkali/alkaline-earth oxide catalysts total oxidation of methane occurs at least partly as a surface process. From the work described in this study, carried out by exposing the catalysts to methane in the absence of oxygen, it may be tentatively derived that this surface process consists of the following consecutive steps when gas-phase oxygen is present:

(1) surface oxidation of methane or methyl radicals to $-\overset{|}{C}-O-$ type products;

(2) surface oxidation of $-\overset{|}{C}-O-$ to compounds containing a $\overset{\diagup}{C}=O$ group, possibly H_2CO;

(3) surface oxidation of H_2CO to surface carbonate or CO_2 by oxygen adsorbed from the gas-phase.

Assuming that the total oxidation of methane is partly a surface process, calcination in methane should, at least to a certain extent, poison the total oxidation sites on the surface and therefore partly suppress this nonselective oxidation. This reasoning is supported by the experiments of Carreiro and Baerns (*9*) and of Mirodatos *et al.* (*29*), who observed an increase in selectivity for C_{2+} hydrocarbons when the catalysts were calcined in the presence of methane before the coupling reaction was carried out.

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