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INFLUENCE OF THE ANION OF PROMOTING SODIUM COMPOUNDS ON THE ACTIVITY AND SELECTIVITY IN OXIDATIVE COUPLING OF METHANE

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The influence of the sodium compound anion–the promoter of the CaO/magnesium-aluminium spinel system–on the activity and selectivity in oxidative coupling of methane has been studied. It is found that the catalysts show optimal properties when the sodium compound of a weak acid is used.

Keywords: Oxidative coupling of methane, methane dimerization, Na^+-$CaO/MgAl_2O_4$ catalyst, anion of sodium compound

1. Introduction

The most recent studies have shown that favourable results have been obtained in oxidative coupling of methane on alkaline earths oxides, promoted by alkaline metal compounds, e.g. Li/MgO or Na/CaO [1–4]. The perspective of utilizing such systems as catalysts will depend on their acquiring the appropriate mechanical resistance that is needed for time consuming work at high temperatures.

Among the various supports, the most favourable features were shown by magnesium-aluminium spinel used in catalysts of hydrocarbons steam reforming [5,6]. This is useful for methane conversion at high temperatures because of the presence of small chemical reactivity, small specific surface area and high mechanical resistance.

In this paper, the results of the studies on CaO/spinel catalysts, promoted by various sodium compounds, are presented.

2. Experimental

The magnesium-aluminium spinel, having a surface area of 1.8 m^2/g, was supplied by the Department of Catalysts of Fertilizer Institute at Pulawy (Poland).

The catalysts containing 10 wt.% of CaO and 1.7 wt.% of Na^+ were prepared by impregnation of the spinel support, crushed to particles in the size of 0.75 to 1.2 mm, with $Ca(NO_3)_2$ solution. After drying, the samples were impregnated again with water solution of sodium compound (NaCl, Na_2SO_4, $Na_4P_2O_7$, NaOH or Na_2CO_3). Atomic absorption spectroscopy (AAS) was used to verify the weight percentages of Na and Ca.

The activity and selectivity of the catalysts were measured at 1023–1073 K (after heating them up in air to an appropriate temperature) in a mixture of CH_4 and air at 1 : 1 volume ratio, under 0.1 MPa pressure, at constant modified contact time $W/F = 0.61\text{–}0.66\ \mathrm{s \cdot g \cdot cm^{-3}}$.

The catalysts showed very good activity and selectivity stability during the lengthy measurements.

3. Results and discussion

The results summarized in table 1 show a very significant influence of the specific promoting sodium compound (i.e. the anion) on the activity and selectivity of the catalysts studied. The influence seems not to depend on the measurement temperature.

Under the same measurement conditions and at constant sodium content (1.6–1.7 wt.% of Na^+ in used samples), the smallest activity is shown by the catalysts containing sodium salts of strong acids (Na_2SO_4 and NaCl).

Several interesting observations concerning the influence of the anion of

Table 1

The activity and selectivity of CaO/magnesium-aluminum spinel catalysts promoted with different sodium salt

Temp. (K)	Promoter	Conversion degree [a] (%)		Selectivity [a] (%)			$\frac{X_{O_2}}{X_{CH_4}}$	$\frac{S_{C_2^=}}{S_{C_2^-}}$	$\frac{S_{CO}}{S_{CO_2}}$	C_{2+} yield (%)	Surface area (m^2/g)
		O_2	CH_4	C_2	C_{3+}	CO_x					
1023	Na_2SO_4	16.2	5.0	77.5	0.9	22.5	3.24	0.42	0.29	3.87	3.79
1073		26.0	10.3	77.5	1.9	21.0	2.52	0.76	0.55	8.14	
1023	NaCl	40.3	9.0	52.0	0.9	48.0	4.47	0.68	0.71	4.76	–
1073		62.0	15.5	54.0	1.5	44.5	3.87	1.00	0.65	8.60	
1023	$Na_4P_2O_7$	46.7	12.0	59.5	1.6	38.0	3.89	0.65	0.21	7.44	2.88
1073		78.3	20.0	58.0	3.4	39.5	3.91	1.19	0.23	12.10	
1023	Na_2CO_3	49.0	11.0	54.5	1.2	44.0	4.45	0.58	0.14	4.84	5.91
1073		82.4	19.2	54.5	2.4	42.5	4.29	0.95	0.13	11.04	
1023	NaOH	46.0	8.1	48.0	0.7	52.0	5.68	0.48	0.12	3.89	–
1073		76.1	16.0	49.5	1.8	48.0	4.75	0.77	0.10	7.68	

[a] Determined with ±0.5% accuracy.

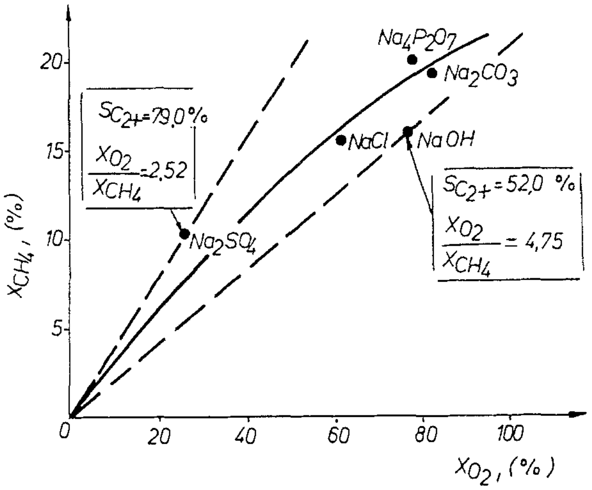

Fig. 1. The influence of O_2 conversion degree (X_{O_2}) on the CH_4 conversion degree (X_{CH_4}) at 1073 K for catalysts promoted by various sodium compounds. Dashed lines indicate the area between both extreme C_{2+} hydrocarbons selectivity ($S_{C_{2+}}$) and X_{O_2}/X_{CH_4}.

sodium promoter on the reaction selectivity arrise from the values of such ratios as oxygen and methane conversion degree (X_{O_2}/X_{CH_4}), selectivity of methane conversion to ethylene and ethane ($S_{C_2^{=}}/S_{C_2^{-}}$) and to carbon oxides (S_{CO}/S_{CO_2}) as given in table 1. Because of the C_{2+} hydrocarbons formed in the reactions utilizing smaller amounts of oxygen per CH_4 molecule than in the combustion processes, the ratio of oxygen and methane conversions reveals the influence of the anion on the changes of the various reaction paths: leading to hydrocarbons (X_{O_2}/X_{CH_4} assumes then low values) or to CO_x (when X_{O_2}/X_{CH_4} is high). The relationship between the conversion degree of CH_4 and the degree of oxygen conversion for the catalysts studied is presented in fig. 1. The dashed lines in fig. 1 indicate the area between the best (Na_2SO_4) and worst (NaOH) promoter for obtaining hydrocarbons (between the highest and the lowest selectivity to C_{2+} hydrocarbons–the lowest and the highest X_{O_2}/X_{CH_4} ratio). Since about the C_{2+} hydrocarbons yield decide simultaneously selectivity as well as the degree of methane conversion, the sodium promoters of CaO/spinel catalyst, in relation to their effectivity, can be ordered in the sequence:

$$Na_4P_2O_7 > Na_2CO_3 \gg NaCl > Na_2SO_4 > NaOH.$$

The properties of the catalyst are different for every promoter used, nevertheless some of the initial sodium compounds may undergo changes during the pretreatment and during catalysis.

As the catalysts with various promoters contain the same amount of sodium and possess different surface areas, the surface Na^+ concentration may differ. However, it seems that neither different surface coverage nor the changes in the specific surface area, caused by introducing various promoters, which were found to be an important factor of controlling C_{2+} hydrocarbons yield [7,8], can elucidate the differences observed among the catalyst properties. The highest efficiency of hydrocarbons formation was obtained in the case of catalysts with the largest and the smallest surface areas and Na^+ coverages.

The sodium promoters applied may be divided into three groups, depending on the anion originate:

1 strong acid–catalyst with small activity is obtained, whereupon the full combustion is small,
2 strong base–high percentage of carbon oxides in the reaction products is observed,
3 weak acid–the catalysts show optimal features: considerable activity with favourable selectivity, i.e., the highest yield of hydrocarbons C_{2+} and the highest ethylene/ethane ratio.

The changes in the activity and selectivity suggest a dependence of CH_4 dimerization on the acid-basic properties of the catalyst surface. Malinowski [9] stated: "The deposition of alkali cations such as alkali hydroxides, carbonates or oxalates was used either for poisoning of acidic centres or producing new basic centres on the surface of greater strength. The properties of the catalyst depend on the kind of alkali ion, on the anion and the temperature of calcination or activation".

According to the studies of Kijeński and Malinowski [10,11], the amount of sodium promoter has a significant influence not only on the distribution of the alkali centres but also of the acid ones in MgO. Iwamatsu et al. [7,12] have found that the amount of the promoter effects the properties of MgO in dimerization of CH_4. This finding is also confirmed by our unpublished data [13] for Na^+-CaO catalyst. Baerns et al. [4] showed the influence of calcination conditions on the activity and selectivity of the $NaOH/Ca(OH)_2$ system.

In our opinion, the results (ours and from the literature [9–11,14,16] presented above suggest a very significant influence of the introduction of various compounds or different amounts of alkali promoters on the equilibrium of the number and strength of basic and acid centres on the surface of metal oxides of alkaline earths, and thereby on their activity and selectivity in oxidative coupling of methane.

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