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INFLUENCE OF VARIOUS PROMOTERS ON THE BASICITY AND CATALYTIC ACTIVITY OF MgO CATALYSTS IN OXIDATIVE COUPLING OF METHANE

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Addition of promoters, such as Li_2O, Na_2O, PbO, La_2O_3, $MgCl_2$ and $CaCl_2$, to MgO causes a large increase in its surface basicity (particularly strong basic sites) and catalytic activity/selectivity in oxidative coupling of methane, but the correlation between the basicity and C_2-yield is poor, indicating that factors other than basicity are also important in deciding catalytic performance.

Promoted MgO catalysts, viz. Li-MgO [1–3], Na-MgO [4,5], PbO-MgO [6,7], $MgCl_2$- and $CaCl_2$-MgO [8,9], La-MgO [10], etc., are being extensively used in the oxidative coupling of methane to C_2-C_2-hydrocarbons. We report here our results showing a large increase in the surface basicity and catalytic activity (in oxidative coupling of methane to C_2-hydrocarbons) of MgO due to addition of the above promoters to it.

Li (7 wt%)-MgO, Na (7 wt%)-MgO, PbO (6 wt%)-MgO, $MgCl_2$ (5 wt%)-MgO, $CaCl_2$ (5 wt%)-MgO and La-MgO (La/Mg = 0.1) were prepared by impregnating powdered hydrated MgO [obtained by heating pure MgO (GR grade) with distilled water on water both for 4 h and drying] with a solution of Li_2CO_3, Na_2CO_3, $Pb(NO_3)_2$, $MgCl_2$, $CaCl_2$ and $La(NO_3)_3$ (respectively), drying, pressing, crushing to particles of 22–30 mesh size and calcining in air at 950 ° C for 10 h. The surface basicity of the catalysts was obtained by measuring the chemisorption of CO_2 at 50 ° C (which gives the total number of basic sites) and at 500 ° C (which gives the number of strong basic sites) using the thermal desorption method described earlier [11], before the catalytic reaction. The oxidative methane coupling reaction was carried out at atmospheric pressure in a conventional flow quartz reactor (i.d.: 10 mm) provided with a Chromel-Alumel thermocouple in the catalyst bed. The catalyst was pretreated in situ in the flow of N_2 (25

Table 1
Influence of promoters on basicity and catalytic activity of promoted MgO catalysts in oxidative coupling of methane

Catalyst	Surface area ($m^2 \cdot g^{-1}$)	Surface basicity		Catalytic activity				
		Total * ($\mu mol \cdot g^{-1}$)	Strong ** ($\mu mol \cdot g^{-1}$)	Total gas flow rate (STP) ($cm^3 \cdot min^{-1}$)	CH_4 conversion (%)	C_2 yield (%)	$\frac{C_2H_4}{C_2H_6}$ ratio	C_2 productivity ($mmol \cdot cm^{-3} \cdot h^{-1}$)
Empty reactor	–	–	–	20	3.2	1.6	0.6	–
				200	0.3	0.1	–	–
MgO	11.3	69.4	1.5	20	5.3	2.7	0.5	2.5
				200	0.9	0.3	–	2.8
Li-MgO	0.2	84.9	30.9	20	8.5	4.5	0.8	4.1
				200	1.4	0.6	0.1	5.5
Na-MgO	1.8	127.2	34.5	20	9.4	3.9	0.8	3.6
				200	1.4	0.4	–	3.7
$MgCl_2$-MgO	13.6	88.0	16.7	20	5.9	3.2	0.7	2.9
				200	1.2	0.4	–	3.7
$CaCl_2$-MgO	4.4	102.3	24.2	20	26.6	15.8	1.4	14.5
				200	11.6	5.2	0.3	47.7
PbO-MgO	10.9	115.0	26.3	20	25.1	16.3	1.0	14.9
				200	19.2	11.6	0.5	106.4
La-MgO	6.3	197.1	26.9	20	23.4	12.0	1.3	11.0
				200	29.2	17.6	1.2	161.4

* Obtained from the chemisorption of CO_2 at 50 ° C.

** Obtained from the chemisorption of CO_2 at 500 ° C.

$cm^3 \cdot min^{-1}$) at 850 °C for 1 h. The feed was a mixture of pure methane and oxygen. The reaction was carried out under the following conditions: amount of catalyst, 0.2 cm^3, CH_4/O_2 ratio, 4.0; total gas flow, 20 or 200 $cm^3 \cdot min^{-1}$; reaction temperature, 800 °C; and time-on-stream, 3 h. The product gases were analysed by an on-line gas chromatograph using Porapak Porapak-Q and Spherocarb columns.

Results on the basicity and catalytic activity of the pure MgO and promoted MgO catalysts are presented in table 1. In the absence of catalyst (i.e. in the empty reactor), the reaction occurs to an appreciable extent only at the lower flow rate. The promoters greatly influence both the surface and catalytic properties of MgO as follows. Because of the addition of promoters to MgO (i) the surface area of the promoted – MgO (except for the promotion by $MgCl_2$) is decreased; the decrease is particularly very large because of the alkali metal promoters, (ii) both the total and strong basic sites are increased; particularly, the increase in the strong basic sites is very large and (iii) the conversion, C_2-yield [i.e. CH_4 conversion (%) X C_2-selectivity (%)/100] and C_2-productivity are also increased; the increase is very large, particularly, for the $CaCl_2$, PbO and La-promoted MgO catalysts. The increase in both the surface basicity and catalytic activity indicates a dependence of the catalytic activity on the basicity. However, the correlation between the basicity and the C_2-yield (table 1) is rather poor. This points to the fact that factors other than basicity are also important in deciding the catalytic performance of the promoted MgO catalysts in oxidative coupling of methane.

It is interesting to note that the PbO-MgO and $CaCl_2$-MgO catalysts show better performance at very high contact time (i.e. at low flow rate). On the contrary, the La-MgO catalyst shows superior performance at a very low contact time and hence it gives very high C_2-productivity. It may be noted that at higher conversions of methane (23–29%) the reaction is limited by oxygen and hence, at higher contact times, the C_2-productivity is expected to be lower.

In conclusion, a large increase in the surface basicity due to the addition of promoters is responsible for the increased catalytic activity/selectivity of the promoted-MgO catalysts in oxidative coupling of methane but factors other than basicity are also important in deciding their catalytic performance.

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