

Oxidative Coupling of Methane on $LnBa_2Cu_3O_{7-x}$ Superconductors

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The superconducting oxides $LnBa_2Cu_3O_{7-x}$ ($Ln=Y, Gd, Er, Yb, Lu$) showed poor selectivity in the oxidative coupling of methane. The addition of 0.5 mol. % Li_2O to these materials considerably enhanced the yield of C_2 hydrocarbons. This effect was related to both lower redox property and higher basicity of Li-doped catalysts as compared to those of undoped ones.

Introduction

Recently high-temperature superconductors have been tested intensively as catalysts for different reactions. The most widely used catalyst is $YBa_2Cu_3O_{7-x}$ (orthorhombic and tetragonal phases and their substituted forms). Reviewing this data, Klissurski and Rives [1] have arrived at the conclusion that the specific activity of superconductors in the complete oxidation reactions is lower than that of non-superconducting related cuprates or of the best total oxidation catalysts (Co_3O_4 , Pt wire).

On the other hand, high efficiency superconductive oxides has been reported for partial oxidation reactions, such as ammoxidation of toluene [2], oxidation of aliphatic alcohols to the corresponding aldehydes [3,4] and oxidation of methane to formaldehyde [5]. In the latter reaction, besides formaldehyde, considerable amounts of carbon oxides were formed. As for C_2 compounds, only a trace amount was detected probably due to the use of N_2O as an oxidant. When oxidizing methane with molecular oxygen over the same $YBa_2Cu_3O_{7-x}$ catalyst, carbon oxides, ethane and ethylene were the main reaction products; no formation of formaldehyde was observed [6]. The selectivity for methane oxidative coupling was strongly dependent on the CH_4/O_2 ratio in the feed. At low partial pressures of oxygen, the catalyst was relatively active in the formation of C_2 hydrocarbons, but at high oxygen partial pressures it preferentially catalyzed the formation of CO_2 . This transition in product selectivity was reversible

In this study we investigated the use of $LnBa_2Cu_3O_{7-x}$ superconductors as catalysts for the oxidative coupling of methane. We also investigated lithium-doped samples, since the presence of alkaline additives in the catalyst normally promotes the occurrence of the oxidative coupling reactions [7].

Experimental

The superconducting oxides $LnBa_2Cu_3O_{7-x}$, when Ln=Y, Gd, Er, Yb, Lu were prepared by grinding together a stoichiometric mole ratio of Ln_2O_3 (ultra-pure grade), $BaCO_3$ (99.3 %) and CuO (99.9%). For the samples doped with 0.5 mol. % Li_2O , the required amounts of Ln_2O_3 , $BaCO_3$, CuO and Li_2CO_3 (analytically pure grade) were mixed and ground. The resulting mixture was heated in air for 12 h at 1023 K, then was pressed into pellets and calcined in air again for 6 h at 1193 K. These materials were gently crushed and sieved in the range 0.5-1.0 mm to provide the reaction.

The electron paramagnetic resonance (EPR) spectra of the catalysts were recorded at 300 K on a Jeol JES-PE-3X spectrometer operating at a band frequency of 9.3 GHz. A DPPH standard was used for calibration.

The catalyst basicity was evaluated by the amount of benzoic acid adsorbed by the catalyst from the solution in dried heptane. The adsorption of benzoic acid was measured spectrophotometrically using a Specord UV-VIS spectrometer.

The catalytic activity in methane oxidation was tested in a continuous flow, fixed bed reactor. All experiments were performed using the feed composition $CH_4/O_2/N_2=30/20/50$ with a total gas flow of 50 ml/ min. Reaction products were analyzed on-line by gas chromatography using columns with Porapak Q and molecular sieve NaX.

Results and Discussion

Methane oxidation on $LnBa_2Cu_3O_{7-x}$ (Ln=Y, Gd, Er, Yb, Lu) superconductors in the 923-1023 K temperature range yielded carbon dioxide, ethane and ethylene as reaction products. The highest total selectivity to C_2 hydrocarbons was obtained with the Yb-containing sample which, however, did not exceed 15%. Other catalyst exhibited even lesser selectivities. These results imply that pure superconducting oxides are poor oxidative coupling catalysts, appearing to be better described as total oxidation catalysts.

The effectivity of $LnBa_2Cu_3O_{7-x}$ oxides with respect to the oxidative coupling of methane increases when modifying them with 0.5 mol. % Li_2O . As is seen from the data listed in Table 1, C_2 selectivities up to 70% were obtained at 923 K and methane conversions lower than 10%. With increasing the conversion, selectivities decreased remaining, however, considerably higher than those observed over unmodified catalysts.

Table 1. Oxidation of methane on Li-doped $LnBa_2Cu_3O_{7-x}$ oxides at contact time 2.4 s

Lanthanide	T (K)	Conversion (%)	Selectivity (%)		
			C_2H_6	C_2H_4	CO_2
Y	923	7.0	17	8.0	75
	973	22	11	12	77
	1023	32	7.6	6.3	86
Gd	923	8.0	37	35	28
	973	11	26	36	39
	1023	19	14	36.4	50.0
Er	923	7.0	40.0	16	44.0
	973	17	17	16	67
	1023	30	8.3	12	80
Yb	923	6.8	21	19	60
	973	23	13	22	65
	1023	28	6.3	22	71.6
Lu	923	6.0	7.6	42	50.4
	973	19	6.2	21	72.5
	1023	20	7.0	14	79

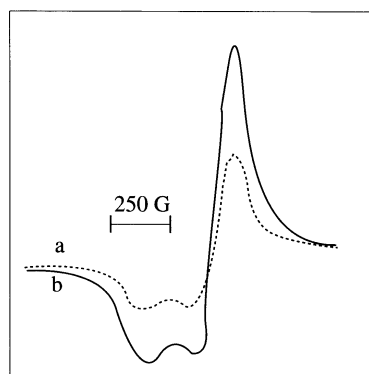


Figure 1. EPR spectra of the original (dotted line) and Li-doped (solid line) $YbBa_2Cu_3O_{7-x}$ oxides

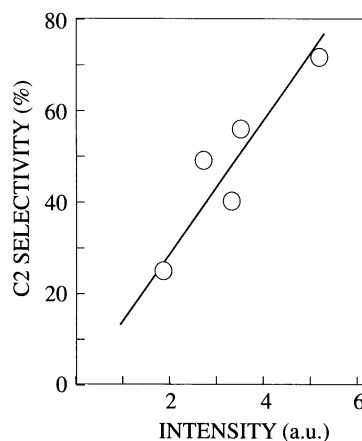


Figure 2. C_2 selectivity at 923 K and methane conversion 6-8 % vs. the intensity of Cu^{2+} signal for Li-modified superconductors

As some authors [1,6] have associated the catalytic activity of $YBa_2Cu_3O_{7-x}$ in total oxidation reactions with the presence of copper we studied its state in catalysts by means of the EPR technique. Figure 1 shows an example of an EPR signal of freshly prepared $YbBa_2Cu_3O_{7-x}$ (spectrum a). Similar signals with axial symmetry typical of copper (II) ions in tetragonal sites were observed for other samples. Used catalysts showed remarkably decreased intensity of the Cu^{2+} signal which was restored by treatment with oxygen. These results suggest that during the catalytic reaction, Cu^{2+} ions could easily be reduced, probably to Cu^+ or Cu^0 , by interaction with methane and reoxidized by oxygen.

Li-doped superconductors also exhibited EPR signals of Cu^{2+} (Figure 1, spectrum b). In comparison with the undoped samples, these were more intense and showed a much smaller decrease in intensity after use in the catalytic reaction. These findings indicate that the Cu^{2+} state is more stable and reduced with difficulty in Li-promoted catalysts. Assuming the stability of Cu^{2+} ions to be proportional to the intensity of their EPR signal, we correlated this parameter with the catalytic performance of modified superconductors. As can be seen in Figure 2, the C_2 selectivity at isoconversion shows a tendency to increase with increasing intensity of the Cu^{2+} signal. This means that the lower the catalyst's redox property to change the copper oxidation state the selectivity for oxidative coupling of methane is higher.

Table 2. Basicity and catalytic activity at 1023 K of original and Li-modified superconductors

Catalyst	Basicity ($\mu\text{mol } C_6H_5COOH/m^2$)	C_2 yield (%)
$YbBa_2Cu_3O_{7-x}$	1.4	1.5
$YbBa_2Cu_3O_{7-x} + Li_2O$	20	8.0
$GdBa_2Cu_3O_{7-x}$	2.4	1.6
$GdBa_2Cu_3O_{7-x} + Li_2O$	22	9.5

When being introduced into the $LnBa_2Cu_3O_{7-x}$, lithium seemed to induce the changes in the electronic state of oxygen ions as well. Since lithium is a more electropositive element than all the metals presented in the original superconductor, its incorporation was expected to increase electrons localization on oxygen ions making them more nucleophilic. This idea was confirmed by the results of the measurements of the catalysts basicity presented in Table 2. Li-doped superconductors showed considerably higher basicity than undoped ones. Respectively, the formers were more active in the oxidative coupling of methane.

Summarizing the data discussed in this paper, we can conclude that the $LnBa_2Cu_3O_{7-x}$ superconductors are poor catalysts for the oxidative coupling of methane due to their redox property in changing the oxidation state of copper. According to Sokolovskii [8], the presence of reduced ions of transition metal promotes the formation of oxygen radical species (O_2^- , O^-) responsible for the oxygenation of hydrocarbons. The addition of small amounts of lithium oxide diminish the redox property and enhance the basicity of the superconductor. Such changes in catalyst properties could facilitate the occurrence of methane mild activation through a heterolytic dissociation of the C-H bond on an active site consisting of the coordinatively unsaturated metal ion (Cu^{2+} or/are Ba^{2+}) and nucleophilic oxygen ion (O^{2-}). This mode of methane activation is believed [7] to take place on the surface of catalysts with basic properties. The Li-modified superconductors studied in this work correspond to this hypothesis.

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