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Influence of Zirconia Preparation on the Selectivity for Oxidative Coupling of Methane

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The oxidative coupling of methane has been studied on various zirconia. ZrO_2 prepared from $ZrCl_4$, $ZrOCl_2 \cdot 8H_2O$, or $ZrO(NO_3)_2 \cdot 2H_2O$ by the addition of ammonium hydroxide showed low selectivity to C_2 compounds (≈9%), whereas ZrO_2 prepared from ammonium hydroxide and potassium hydroxide produced relatively high selectivities (up to 47%) together with an approximately similar conversion as that found with the ammonia-treated ZrO_2 (ca. 10% of methane conversion) at 775°C. When LiOH or NaOH was employed in place of KOH, the selectivity was as low as 8%. The high selectivity to C_2 compounds on ZrO_2 may be attributed to two factors: a small quantity of surface potassium and the presence of surface hydroxyl groups.

INTRODUCTION

Zirconia (ZrO_2) possesses acidic, basic, oxidizing, and reducing properties (*1*, *2*) and has been studied as a catalyst in various reactions (*3–6*). ZrO_2 exhibits three polymorphic forms, the monoclinic, tetragonal, and cubic phases. Although the monoclinic phase is stable below 1170°C, the tetragonal phase may be stabilized at lower temperature under certain conditions. Recently Davis and co-workers (*7*) have shown that tetragonal ZrO_2 can be obtained selectively from a zirconium chloride solution by the addition of NH_4OH and KOH, followed by washing to pH = 7 and calcination at 500°C, in contrast to that prepared by the addition of NH_4OH which yields only the monoclinic phase. Although not detected by XRD (*7*), a trace amount of potassium may be present in the tetragonal ZrO_2 prepared with KOH (*8*).

Although ZrO_2 has been widely employed as a catalyst in various reactions (*9*) earlier work on the use of ZrO_2 for the oxidative coupling of methane is relatively sparse (*10–17*). ZrO_2 has been reported to be relatively inactive, as compared to various oxides, for the coupling process, with very high selectivity to C_1 species (*10*, *13*). The use of ZrO_2 as a support in the coupling process has also been reported (*12*, *14*). In one of these (*14*), relatively high conversions and C_2 selectivities were obtained with 10% Li_2O, Na_2O, or K_2O–ZrO_2. In a recent paper (*15*), ZrO_2 has been used as a promoter for Li/MgO to improve the activity of the unpromoted catalyst. In our previous paper (*16*), ZrO_2 prepared from $ZrCl_4$ solution by the addition of NH_4OH was employed to show that the catalytic performance at a relatively low temperature (less than 600°C) strongly depended on the preparation procedure, and C_2H_6 was formed even at a temperature of 530°C.

The catalytic performance of ZrO_2 has been generally known to be strongly dependent on the preparation procedures as reported in the catalytic conversion of alcohol

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(*6*), the CO–H_2 reaction (*5*) and most recently, in a paper appearing after the submission of the present report, the oxidative coupling of methane over alkali metal chloride promoted zirconia (*17*). Since the pioneering work of Keller and Bhasin (*18*) on the oxidative coupling of methane was first published, a wide variety of oxide catalysts has been examined. Although a number of minor components has been tested as additives with many of these oxides, in an effort to enhance catalytic performance, lithium and sodium have been found to be two of the most advantageous, with the remainder of the alkali metals generally considerably less beneficial (*10, 19*). The present work examines the effect of the preparative reagents on the catalytic properties of the ZrO_2 and, in particular, demonstrates that ZrO_2 modified with potassium has considerably enhanced catalytic capabilities in the methane conversion process, in contrast with those found with ZrO_2 modified with lithium or sodium.

EXPERIMENTAL

Apparatus and Procedure

The catalytic experiments were performed in a fixed-bed continuous flow reactor operated under atmospheric pressure. The reactor consisted of a 9-mm-I.D. and 35-mm-length quartz tube sealed at each end to 4-mm-I.D. quartz tubes to produce a total length of 25 cm. The catalyst (1.4 g) was held in place in the enlarged portion of the reactor by two quartz wool plugs. The reactor was designed to minimize the free volume in the hottest zone so as to reduce the contribution of noncatalytic homogeneous reactions. In the empty reactor or the reactor filled with quartz wool, the methane conversion at 800°C was 0.52 or 0.63%, respectively. In all experiments, the temperature of the catalyst was raised to 775°C while maintaining a continuous flow of helium, and was then conditioned at this temperature under 25 ml/min flow of molecular oxygen for 1 h. The reactor was then purged with helium and its temperature was adjusted to that for the reaction before introduction of the reactant gas mixture consisting of methane (8.5 ml/min), oxygen (1.2 ml/min), and helium (20.3 ml/min).

Analysis

The reaction was monitored with an on-stream Shimadzu GC-8APT gas chromatograph with a TC detector and integrator (Shimadzu C-R6A). Two columns, one Porapak N (6 m × 3 mm ø, programmed 45–150°C), the other Molecular Sieve 5A (20 cm × 3 mm ø, 45°C) were employed in the analyses. The methane conversion was calculated from the products and the methane introduced in the feed. The selectivities were calculated from the conversion of methane to each product on a carbon base.

Catalyst Preparation

Hydrous zirconium oxide (with no alkaline treatment) was precipitated from a $ZrCl_4$, $ZrOCl_2 \cdot 8H_2O$, or $ZrO(NO_3)_2 \cdot 2H_2O$ solution (Wako Pure Chemicals, Osaka; 0.3 *M*, 250 ml) by the rapid addition of concentrated NH_4OH to produce a solution which possessed the final pH of 10.3–10.6, following the procedures proposed by Davis and co-workers (*7*). When hydrous zirconium oxide with KOH treatment was desired, a potassium hydroxide solution (4 *M*) was added to the solution of pH = 10.3–10.6 to produce a solution with a final pH of 13.5–14.0. In all cases the hydrous zirconium oxide was collected by filtration and washed with water to a pH of 7 and the absence of detectable Cl^- (when $ZrCl_4$ and $ZrOCl_2$ were employed as reactants). The hydrous oxide was dried in air at 100°C overnight and calcined at 500°C for 5 h. For convenience, each zirconia thus obtained a pH = 10.3–10.6 and pH = 13.5–14.0 will be denoted as Cl_4-10, OCl_2-10, and N-10 and Cl_4-14, OCl_2-14, and N-14, respectively, based on the zirconium source and pH. ZrO_2 treated with LiOH or NaOH was prepared from $ZrOCl_2 \cdot 8H_2O$ by the same procedure as above except using LiOH or NaOH and denoted as OCl_2-Li or OCl_2-Na, respectively. As a reference, commercial ZrO_2 (Wako, GR-grade) dissolved in water, filtered, dried, and calcined in the same manner as above and denoted as ZrO_2-C. Particle sizes of 10–20 mesh were employed in the investigations.

Characterization of Catalysts

The surface areas of the catalysts were measured with a conventional BET nitrogen adsorption apparatus (Shibata P-700, Tokyo).

Powder X-ray diffraction (XRD) patterns were recorded with MXP-18 of MAC Science Co. using monochromatized Cu*Kα* radiation. Patterns were recorded over the range $2\theta = 5°–90°$. Each catalyst prepared in the present work was a mixture of monoclinic and tetragonal phases. The molar % of tetragonal phase (%T) was calculated from the ratio of the peak intensities (*7*),

$$(1,1,1)_T/[1.6 \times (1,1,-1)_M + (1,1,1)_T],$$

where T and M denote tetragonal and monoclinic phases, respectively. The average particle size of the catalyst was determined from Scherrer's equation (*20*).

Surface analyses by X-ray photoelectron spectroscopy (XPS) were carried out with a Perkin–Elmer-Phi 5500 spectrometer using unmonochromatized Mg*Kα* radiation. The binding energies were corrected using 285.0 eV for the C 1*s* level, resulting from contaminant carbon, as an internal standard. The XPS spectra were measured at room temperature without any additional surface treatment.

The content of potassium in the catalyst was measured as follows. The catalyst (1 g) was dissolved in conc. HCl (10 ml) and left overnight. The solution was diluted with distilled water to a pH of 1.2 and filtered. Inductivity coupled plasma (ICP) analyses for the filtered solutions were made with a sequential plasma spectrometer (Shimadzu ICPS-5000).

RESULTS AND DISCUSSIONS

Physical Properties of Each ZrO_2

The physical properties of each ZrO_2 prepared are summarized in Table 1. As observed from XRD, each ZrO_2 consisted of two polymorphic forms, the monoclinic and tetragonal phases. The ratio of the two phases strongly depended on the procedure employed for the preparation of the catalyst. ZrO_2 treated with no alkali hydroxides (Cl_4-10, OCl_2-10, and N-10) showed similar values of surface area, crystal size and the ratio of the two phases. A high ratio of the tetragonal phase in ZrO_2 was observed in those prepared from $ZrCl_4$ and $ZrO(NO_3)_2 \cdot 2H_2O$ with KOH treatment (Cl_4-14 and N-14), while the ratio of two phases in OCl_2-14 was quite low. The high content of the tetragonal phase in Cl_4-14 and N-14 is in agreement with the results of Davis and co-workers (*7*). Even when LiOH or NaOH was used in place of KOH, the ratio of the tetragonal phase in ZrO_2 prepared from $ZrOCl_2 \cdot 8H_2O$ (OCl_2-Li and OCl_2-Na) was not improved.

TABLE 1

Physical Properties of ZrO_2

Catalyst	BET area (m^2/g)	Crystal size (nm)	%T[a]	Bulk density[b] (g/cm^3)
ZrO_2-C	22.2	11	4	0.92
Cl_4-10	66.4	5	3	1.27
Cl_4-10[c]	22.2	10	3	—
Cl_4-14	72.7	6	65	1.55
Cl_4-14[c]	17.9	11	1	—
OCl_2-10	62.7	5	2	1.40
OCl_2-14	71.6	4	7	1.47
N-10	68.0	4	5	1.40
N-14	68.7	5	56	1.47
OCl_2-Li	65.9	5	9	1.17
OCl_2-Na	60.6	5	8	1.17

[a] Molar % of tetragonal phase (remainder; monoclinic phase based on XRD).

[b] Mesh size of catalysts is 10–20.

[c] After reaction (6 h on-stream) at 775°C.

ZrO_2 without KOH Treatment

In all catalytic experiments, the products were CO, CO_2, C_2H_4, and C_2H_6. Water and hydrogen were also produced but are not reported here. The conversion of oxygen was virtually constant during 6 h on-stream at approximately 98%. Excellent carbon balances (100 ± 2%) were obtained on each catalyst. The conversions and selectivities at 775°C with a CH_4/O_2 feed ratio of 7.1 on

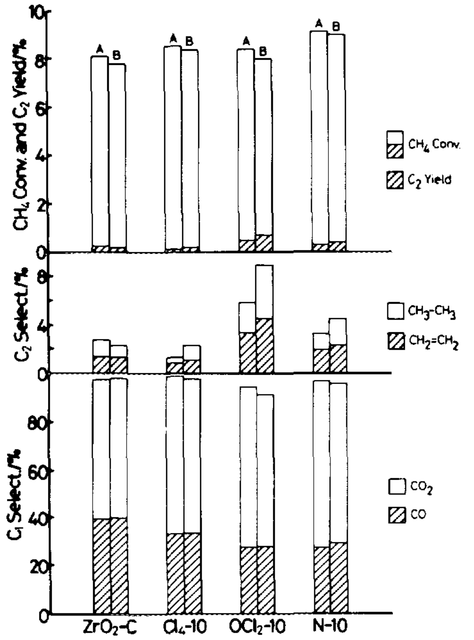

FIG. 1. Methane conversion on ZrO_2 without KOH treatment at 775°C (O_2 conversion $\geq$ 98%). Reaction conditions: CH_4 215 Torr and O_2 30.4 Torr diluted with He. Total flow rate: 30 ml/min. Weight of catalyst: 1.4 g. Symbols: (A) 0.5 h on-stream and (B) 6 h on-stream.

Cl_4-10, OCl_2-10, and N-10 at 0.5 and 6 h on-stream are shown in Fig. 1, together with that on commercial ZrO_2-C. Methane conversion on each catalyst differed very little (8–9%) and C_1 species were obtained with more than 90% selectivity. It is of interest that C_2 selectivity on OCl_2-10 was approximately twice that observed on ZrO_2-C, Cl_4-10, and N-10. Although a Cl^- test with $AgNO_3$ for OCl_2-10 was negative, the possibility of the presence of a trace amount of the oxychloride in the catalyst cannot be excluded. It has been found that oxychlorides in some catalyst systems play an important role in the improvement of C_2 selectivity and CH_4 conversion (*21*, *22*). Since any $ZrCl_4$ remaining in Cl_4-10 would undoubtedly be vaporized (sublimation temperature of $ZrCl_4$ is 437°C) under the present reaction conditions, the C_2 selectivity on Cl_4-10 may be taken as similar to that on ZrO_2-C and N-10. The surface area and crystal size of Cl_4-10 changed during 6 h on-stream (Table 1), which suggests that sintering of the catalyst occurred during reaction, but the conversion of methane and C_2 selectivity changed relatively little (Fig. 1). These observations provide support for the supposition that the reaction behaviour is essentially independent of the surface area. The ratio of the monoclinic phase in Cl_4-10 was virtually constant during the reaction as expected from the thermodynamic stability of this phase at the reaction temperatures (Table 1).

ZrO_2 with KOH Treatment

Over ZrO_2 treated with KOH the catalytic performance was considerably improved in comparison with those catalysts not treated with KOH (Fig. 2). The conversion of methane increased in the order ZrO_2-C < Cl_4-14 < OCl_2-14 < N-14 at 0.5 h on-stream with a small amount of deactivation observed on each treated catalyst. The C_2 selectivity was also improved with KOH treatment, partic-

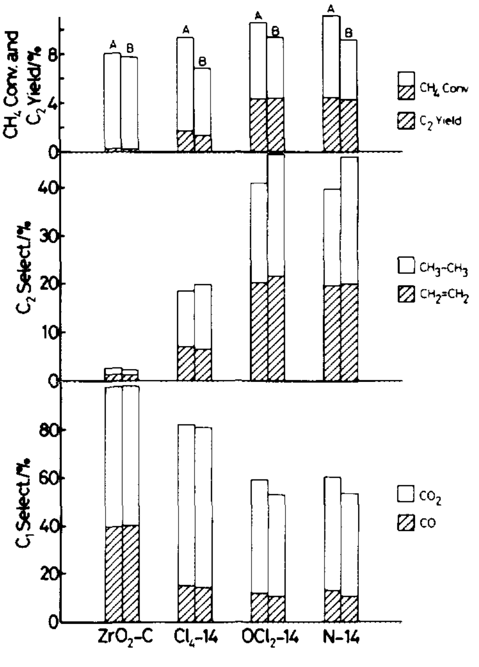

FIG. 2. Methane conversion on ZrO_2 with KOH treatment at 775°C (O_2 conversion $\geq$ 98%). Reaction conditions and symbols as in Fig. 1.

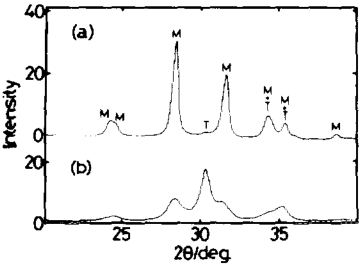

FIG. 3. The XRD patterns for Cl_4-14 after reaction for 6 h at 775°C (A) and before reaction (B). Reaction conditions as in Fig. 1. Symbols: (M) monoclinic phase and (T) tetragonal phase.

ularly on OCl_2-14 and N-14, for which the C_2 selectivity was approximately 5–10 times that on OCl_2-10 and N-10. The surface area and crystal size of Cl_4-14 changed markedly during 6 h on-stream, as shown in Table 1. Moreover, the tetragonal phase in Cl_4-14 (%T = 65) was completely converted to the monoclinic phase (Fig. 3), although the catalytic performance, in particular the C_1 and C_2 selectivities on Cl_4-14 remained almost unchanged during 6 h on-stream (Fig. 4). These results suggest that neither the phase composition nor the BET surface area is a decisive factor in improving the C_2 selectivity on the catalyst which has been treated with KOH.

In the present procedure for the catalyst preparation alkali metal may be incorporated into ZrO_2, since hydrous zirconium (IV) oxide before calcination has been reported to be an ion-exchanger for transition metals, alkaline earth metals, and alkali metals (*8*). ICP analysis for K^+ in Cl_4-14, OCl_2-14, and N-14 showed that small amounts of potassium were present in each ZrO_2 (ca. 3.3, 3.5, and 3.1 mg K^+/g-ZrO_2, respectively).

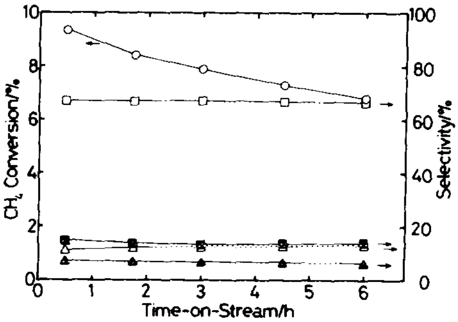

FIG. 4. CH_4 conversions, C_2 selectivity, and C_1 selectivity on Cl_4-14 for various times on-stream up to 6 h at 775°C (O_2 conversion ≥ 98%). Reaction conditions as in Fig. 1. Symbols: (○) CH_4 conversion, (△) CH_3–CH_3 selectivity, (▲) CH_2=CH_2 selectivity, (□) CO_2 selectivity, and (■) CO selectivity.

XPS analysis was used to compare the catalyst surface of ZrO_2-C, OCl_2-10, and OCl_2-14. As shown in Table 2, the binding energy of Zr $3d_{3/2}$, Zr $3d_{5/2}$, C 1*s*, and O 1*s* for each catalyst were observed at almost the same position. In the spectrum of C 1*s* for OCl_2-10 and $OCl_2$14, peaks at 289.0 and 289.1 eV, respectively, were observed and could be attributed to CO_3^{2-} (*23*). Two peaks at 293.0 and 296.2 eV not found for the remaining samples were observed in the spectrum for OCl_2-14 (Table 2). These peaks may be attributed to K $2p_{3/2}$ and K $2p_{1/2}$ for K^+, respectively (*24*). Unfortunately, the counter anion of K^+ on the catalyst cannot be identified, because the binding energies of many K compounds differ relatively little from each other around 293.0 eV for K $2p_{3/2}$ (*24*) and K^+ is present in small quantities. However it is evident that the oxidative coupling of methane may be enhanced by the potassium present on the ZrO_2 catalyst. The nature of the counter cation for CO_3^{2-} in OCl_2-10 and OCL_2-14 is unclear, but it appears that the influence of CO_3^{2-} in the oxidation process is negligible since similar activities are observed with ZrO_2-C and OCl_2-10.

Promotion of the oxidative coupling of methane with alkali metals has been studied especially with lithium-doped magnesia (*25*) and sodium-doped calcium oxide (*26*), and related catalysts (*15*). In those systems, the replacement of alkaline earth metal by alkali metal can take place due to the similar radii of both cations, as in the cases of Li^+ (0.68 Å) and Mg^{2+} (0.66 Å) and Na^+ (0.97 Å) and Ca^{2+} (0.99 Å) (10.25). In the present system, potassium cannot be doped in such a man-

TABLE 2

Summary of XPS Analyses for ZrO_2-C, OCl_2-10, and $OCl_2$14

Sample	Binding energy (eV)						
	Zr		C 1*s*		O 1*s*	K	
	$3d_{3/2}$	$3d_{5/2}$	C	CO_3^{2-}		$2p_{3/2}$	$2p_{1/2}$
ZrO_2-C	184.4	182.2	285.0	+[a]	530.0	—	—
OCl_2-10	184.7	182.3	285.0	289.1	530.1	—	—
OCl_2-14	184.6	182.2	285.0	289.0	530.0	293.0	296.2

[a] Trace.

ner, because the radius of K^+ (1.33 Å) is quite different from that of Zr^{4+} (0.80 Å). As pointed out in our previous paper (*16*), the surface hydroxyl groups on ZrO_2 appear to be closely related to the active sites for the oxidative coupling of methane. In the present system, the hydroxyl group also plays an important role in the zirconia catalysts containing potassium. The protons in the hydroxyl groups of the hydrous zirconium oxide before calcination have ion-exchange capacity for transition metals, alkaline metals, and alkali metals. Therefore, potassium may be incorporated in and on the catalyst during the preparation through ion-exchange to form an active site on ZrO_2. Although active species and active sites unfortunately cannot be identified due to the small quantities of potassium, an ion-exchange process during the preparative stage may lead to potassium substitution in the catalyst. It is important to note that the introduction of KOH into the preparative process undoubtedly increases the surface pH of the resulting solid and hence the concentration of surface hydroxyl groups. Since earlier work from one of our laboratories demonstrated the importance of surface hydroxyl groups on ZrO_2 in the methane conversion process any variation in the ZrO_2 preparation process which leads to an increase in the surface pH undoubtedly directly contributes to the catalytic properties of the resulting solid (*16*). It is difficult, at this time, to disentangle the effect of the introduction of small quantities of the alkali metal from the influence of surface hydroxyl groups on the properties of ZrO_2 in the methane conversion process.

Comparison of the catalytic performance at 775°C with that at 700 and 835°C on each KOH-treated ZrO_2 catalyst shows that C_2 selectivity reached a maximum at 775°C while CH_4 conversion was not affected by the reaction temperature (Fig. 5). The order of C_2 selectivity for the three catalysts increased in the approximate order Cl_4-14 < OCl_2-14 < N-14. Since both the bulk K/Zr ratio determined by ICP analysis and the K/Zr ratio on the catalyst surface determined by XPS do not depend on the preparative method (Table 3), the selectivity is apparently not directly dependent on the potassium content. However, the quantity of surface K^+ on each catalyst was almost twice that of bulk K^+. Quantitatively similar behaviour has been found with sodium-doped La_2O_3 catalyst (*23*). There is no evidence of structure sensitivity of the catalyst from the present data since no correlation between the selectivity and phase composition is evident (Table 1). It is, of course, possible, as has been found in other catalytic reactions (*5*, *6*) that the source of the zirconia has an influence on the activity and selectivity in the methane coupling process.

ZrO_2 with LiOH and NaOH Treatment

It is of interest to examine LiOH- or NaOH-treated ZrO_2 catalysts, because

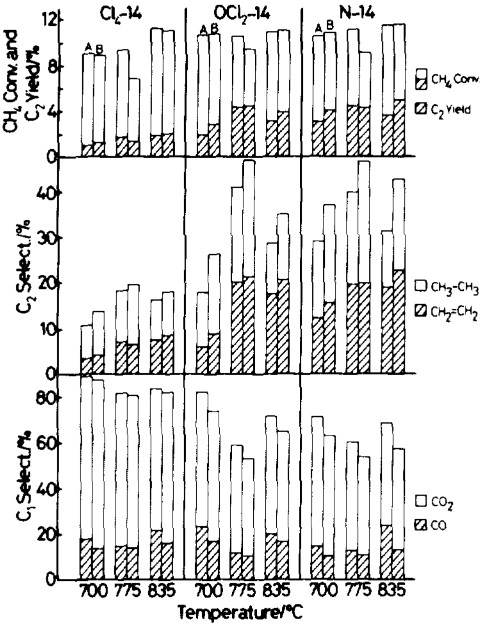

FIG. 5. The effect of temperature in the conversion of CH_4 and selectivities to C_1 and C_2 on ZrO_2 with KOH treatment (O_2 conversion $\geq 98\%$). Reaction conditions as in Fig. 1 except for the reaction temperature. Symbols as in Fig. 1.

many Li- or Na-doped catalyst systems show high methane conversion and C_2 selectivity. However, C_2 selectivities on OCl_2-Li and OCl_2-Na were quite low, compared to that on OCl_2-14, although they are approximately twice that on commercial ZrO_2-C (Fig. 6). XPS analysis for OCl_2-Li and OCl_2-Na revealed the presence of relatively small quantities of alkali on the catalyst surface (Table 3). In general the ability of alkali cations to ion-exchange from the aqueous phase follows the order $Rb^+ > K^+ > Na^+ > Li^+$, that is, the inverse of the radii of the hydrated alkali cations (*27*). Thus the absence of any significant improvement in selectivity found with OCl_2-Li and OCl_2-Na may be attributed at least in part, to the relatively small quantities of Li and Na found in these catalysts. In contrast to the aforementioned, on zirconia-supported Li_2O, Na_2O, or K_2O catalyst (10% loading), it has been reported that the order of C_2 selectivity increased in the order $Li_2O/ZrO_2 < K_2O/ZrO_2 < Na_2O/ZrO_2$ (28, 37, and 44%, respectively) (*14*). The chemical nature of the present catalyst surface is expected to be significantly different from that of the

TABLE 3

Alkali:Zr Atomic Ratios

Sample	K/Zr		Na/Zr[b]	Li/Zr[b]
	Bulk[a]	Surface[b]		
Cl_4-14	0.004_5	0.011	—	—
OCl_2-14	0.004_7	0.013	—	—
N-14	0.004_2	0.009	—	—
OCl_2-Li	—	—	—	ND[c]
OCl_2-Na	—	—	<0.003	—

[a] By ICP.
[b] By XPS.
[c] Not detected.

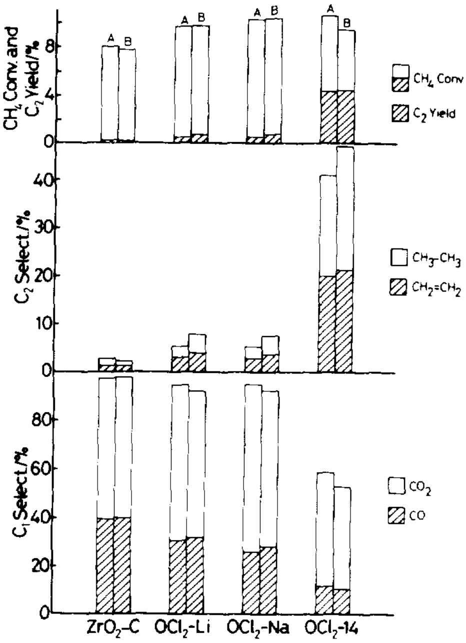

FIG. 6. The effect of alkali hydroxide treatment for ZrO_2 on membrane conversion (O_2 conversion $\geq 98\%$). Reaction conditions and symbols as in Fig. 1.

systems in which alkali oxides are deposited on zirconia.

CONCLUSION

The presence of a trace amount of potassium cation on zirconia doped by ion-exchange plays an important role in the promotion of the oxidative coupling of methane on the catalyst. The improvement of the selectivity on the present catalyst appears to be related to the ion-exchange properties of the alkali cation, but the effect of the increase in the numbers and strength of surface hydroxyl groups cannot be discounted.

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