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Effect of Potassium-Treated Zirconia on the Oxidative Coupling of Methane

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Various zirconia were prepared from $ZrOCl_2\cdot 8H_2O$ by the addition of aqueous ammonia and potassium hydroxide; the effect of the catalyst preparation on the oxidative coupling of methane over zirconia was studied. The selectivity to such C_2 compounds as ethylene and ethane was strongly influenced by the pH of the preparative solution of $ZrOCl_2\cdot 8H_2O$, NH_3 aq, and KOH, as well as the sequence of the addition of each hydroxide during the preparation of the catalyst.

The effects of the introduction of gas-phase additives[1—6)] and solid-phase additives[7,8)] on the oxidative coupling of methane have been studied in our laboratories. Over zirconia (ZrO_2) treated with KOH, an increased selectivity to C_2 compounds, such as ethylene and ethane, was observed,[7)] although ZrO_2 has been reported to be relatively inactive for the coupling process, with a very high selectivity to CO and CO_2.[9,10)] Since the improvement in the selectivity on ZrO_2 treated with KOH may be related to the ion-exchange properties of the potassium cation, the chemical nature of this catalyst may significantly differ from that of ZrO_2, on which potassium species have been deposited.[7)] However, earlier work of one of our laboratories demonstrated the importance of the surface hydroxyl groups on ZrO_2 based on the mechanism for the coupling reaction.[11)] Thus, the catalytic properties of ZrO_2 could be improved through the introduction of KOH during the preparation of the catalyst as a result of increases in the surface pH of the resulting solid and, hence, the concentration of the surface hydroxyl groups.[7)]

ZrO_2 has been widely employed as a catalyst in various reactions.[12)] Khan and Ruckenstein recently reported the oxidative coupling of methane over ZrO_2 to which alkali metals, in one form to another, have been added.[13,14)]

The present work examined the oxidative coupling of methane over ZrO_2 treated with KOH, with particular regard to understanding the separate effects of introducing small quantities of potassium and the influence of the surface hydroxyl groups. Furthermore, the methane coupling reactions over K_2CO_3/ZrO_2 and KOH/ZrO_2 were also studied in order to illustrate the differences in catalytic properties of potassium-deposited and potassium-exchanged ZrO_2.

Experimental

The catalytic experiments were performed in a fixed-bed continuous-flow reactor operated under atmospheric pressure. The reactor comprised a 9 mm i.d., 35 mm long, 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, 10—20 mesh) was held in place in the enlarged portion of the reactor by two quartz wool plugs. The reactor was designed so as to minimize the free volume in the hottest zone, thus reducing the contribution of noncatalytic homogeneous reactions. In all experiments, the temperature of the catalyst was raised to 775 °C while maintaining a continuous flow of helium. The catalyst was then conditioned at this temperature under a 25 $\mathrm{ml\,min^{-1}}$ flow of molecular oxygen for 1 h. Following this, the reactor was purged with helium and a reactant gas mixture comprising methane (8.5 $\mathrm{ml\,min^{-1}}$), oxygen (1.2 $\mathrm{ml\,min^{-1}}$), and helium (20.3 $\mathrm{ml\,min^{-1}}$) was introduced into the reactor. 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 ϕ, programmed 45—150 °C), the other Molecular Sieve 5A (20 cm×3 mm ϕ, 45 °C)) were employed in the analyses. The methane conversion was calculated based on the products and the methane introduced into the feed. The selectivities were calculated based on the conversion of methane to each product on a carbon base.

ZrO_2 was prepared by procedures proposed by Srinivasan et al.[15)] Hydrous zirconium oxide was precipitated from an aqueous solution of $ZrOCl_2\cdot 8H_2O$ (Wako Pure Chemicals, Osaka; 0.3 M, 250 ml) (1 M=1 $\mathrm{mol\,dm^{-3}}$) by a rapid addition of 15 M NH_3 aq (75 ml) to produce a solution of $\mathrm{pH}\approx 10.5$. When preparative solutions of $\mathrm{pH}\approx 11.5$, 12.5, and 13.5 were desired for the KOH-treated hydrous zirconium oxide, a potassium hydroxide solution (4 M; 12.5, 40, and 100 ml, respectively) was added to a solution of $\mathrm{pH}\approx 10.5$. In all cases the hydrous zirconium oxide was collected by filtration and washed with water to a pH of 7 and without detectable Cl^-. The hydrous oxide was dried in air at 100 °C overnight and calcined at 500 °C for 5 h. For convenience, each ZrO_2, thus obtained, with pH values equal to 10.5, 11.5, 12.5, and 13.5 are denoted as ZrO_2-10, ZrO_2-11, ZrO_2-12, and ZrO_2-13, respectively. Two additional samples of hydrous zirconium oxide were prepared by the addition of a mixture of NH_3 aq (75 ml) and 4 M KOH (100 ml), or the addition of 4 M KOH (100 ml) followed by that of NH_3 aq (75 ml) to the $ZrOCl_2\cdot 8H_2O$ solutions (0.3 M, 250 ml). Each hydrous zirconium oxide was treated using the same procedure as mentioned above to give ZrO_2, which is denoted as ZrO_2-13T or ZrO_2-13R, respectively. The catalysts KOH/ZrO_2 and K_2CO_3/ZrO_2 were prepared by the addition of aqueous solutions containing appropriate amounts of KOH or K_2CO_3 to the hydrous zirconium oxide solutions, which were prepared from $ZrOCl_2 \cdot 8H_2O$ and NH_3 aq and washed to neutral, at 80—90 °C with stirring followed by drying in air at 100 °C overnight. The catalysts were finally calcined at 500 °C for 5 h. The loadings of potassium species in the catalysts were determined by X-ray fluorescence analysis (Rigaku, Osaka, 3370 X-ray spectrometer), and are expressed as mol %.

The surface areas of the catalysts were measured with a conventional B.E.T. nitrogen adsorption apparatus (Shibata P-700, Tokyo). Powder X-ray diffraction (XRD) patterns were recorded with an MXP-18 of MAC Science Co. using monochromatized Cu $K\alpha$ radiation. The patterns were recorded over the range $2\theta = 5$—90 degrees. The average particle size of the catalyst was determined from Scherrer's equation.[16] Surface analyses by X-ray photoelectron spectroscopy (XPS) were carried out with a Perkin Elmer-Phi 5500 spectrometer using Mg $K\alpha$ radiation. The binding energies were corrected by using the 1s level (285.0 eV) for contaminant carbon as an internal standard. The XPS spectra were measured at room temperature without any additional surface treatment.

Results and Discussion

Physical Properties of ZrO_2 Treated by KOH, K_2CO_3/ZrO_2 and KOH/ZrO_2. The physical properties of prepared KOH-treated ZrO_2 are summarized in Table 1, together with that of ZrO_2 without a KOH treatment (ZrO_2-10). As observed from XRD (Fig. 1), each ZrO_2 prepared in the present work was a mixture of monoclinic and tetragonal phases. It is of interest that the monoclinic phase in ZrO_2-10 is completely converted to the tetragonal phase by treating with a KOH solution; the relative amounts of the tetragonal phase in ZrO_2-11, ZrO_2-12, and ZrO_2-13, however, decreased upon using increasing quantities of the KOH solution. Although the volume of the KOH and NH_3 aq solutions employed in the preparation of ZrO_2-13, ZrO_2-13R, and ZrO_2-13T were similar, the phase compositions in those samples were dissimilar. It should be noted that earlier work showed that the surface area, crystal size, and relative amounts of the monoclinic and tetragonal phases in the ZrO_2 catalyst have little or no influence on the methane coupling reaction.[7,11] The effects of the loading of potassium compounds on the surface area and bulk density of K_2CO_3/ZrO_2 and KOH/ZrO_2 are summarized in Table 2. The surface area of each catalyst increased with decreasing loading.

Table 1. Physical Properties of ZrO_2

Catalyst	BET area	Crystal size	Bulk density	K/Zr[a]
	$m^2\,g^{-1}$	nm	$g\,cm^{-3}$	
ZrO_2-10	63	5	1.40	0
ZrO_2-11	111	6	1.27	0.016
ZrO_2-12	113	4	1.40	0.011
ZrO_2-13	72	4	1.47	0.013
ZrO_2-13R	139	4	1.40	0.023
ZrO_2-13T	119	5	1.40	0.015

a) Atomic ratio on the surface determined by XPS.

Effect of pH in the Preparation Stage on Methane Coupling. In all catalytic experiments the products were CO, CO_2, C_2H_4, and C_2H_6. Although water and hydrogen were also produced, they are not reported here. The conversion of oxygen was virtually constant during 6 h on-stream at approximately 98%, except that found with ZrO_2-13R at 94%. The methane conversions and selectivities to C_1 and C_2 compounds on ZrO_2-10, ZrO_2-11, ZrO_2-12, and ZrO_2-13 at 0.5 and 6 h on-stream are given in Fig. 2. Methane conversion on each catalyst showed relatively little change with the preparative pH. However, the selectivity to C_2 compounds increased significantly with increasing pH, that is, with an increase in the amount of 4 M KOH solution employed in the preparation. It is important to note that the introduction of KOH in the preparation undoubtedly increases the surface pH of the resulting solid and, hence, the concentration of the surface hydroxyl groups.[7] Since earlier work from one of our laboratories demonstrated the importance of the surface hydroxyl groups on ZrO_2 in the methane coupling process, any variation in the ZrO_2 preparation process leading to an increase in the surface pH undoubtedly contributes directly to the catalytic properties of the resulting solid.[11] Furthermore, in the present procedure for the preparation of ZrO_2, potassium 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.[17] XPS analyses were used to compare the catalyst surfaces of ZrO_2-10, ZrO_2-11, ZrO_2-12, and ZrO_2-13. The binding energies of Zr $3d_{3/2}$, Zr $3d_{5/2}$, C 1s, and O 1s for each catalyst were observed at approximately similar energies of 185, 182, 285, and 530 eV, respectively.[18] Two peaks at 293 and 296 eV with trace areas were observed in the spectrum for each ZrO_2, except for ZrO_2-10. These peaks may be attributed to K $2p_{3/2}$ and K $2p_{1/2}$ for K^+, respectively.[18] Although the very small quantities of potassium species on the catalyst did not permit accurate XPS analyses, there is evidence that the K/Zr ratio on the catalyst surface increased with increasing pH (Table 1). Therefore the improvement in the C_2 selectivity with increasing pH may be attributed to one or both of two factors: the presence of surface hydroxyl groups and a small quan-

Table 2. Surface Area and Bulk Density of ZrO_2-Supported Catalysts

Catalyst	K_2CO_3/ZrO_2			KOH/ZrO_2		
loading/%[a]	10	2.4	0.5	10	2.4	0.5
Surface area/$m^2\,g^{-1}$	84	101	123	68	99	130
Bulk density/$g\,cm^{-3}$	1.27	1.27	1.17	1.27	1.17	1.08

a) Determined by X-ray fluorescence analysis.

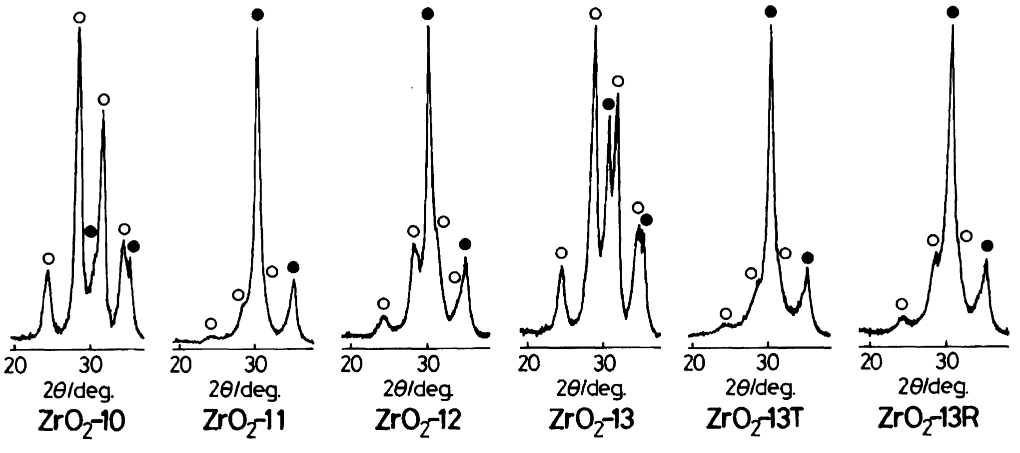


Fig. 1. XRD patterns for ZrO_2 prepared with various procedures. Symbols: ○, Monoclinic phase. ●, Tetragonal phase.

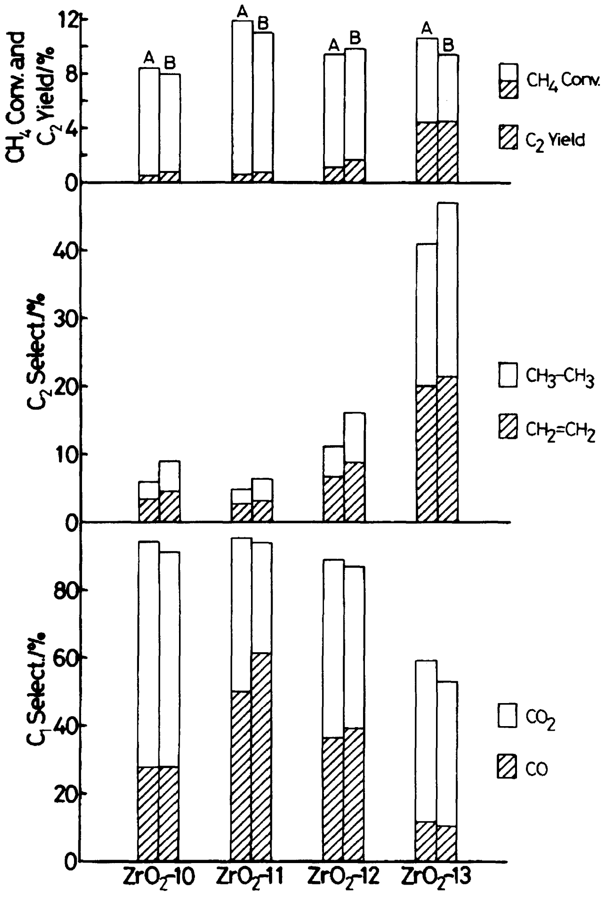
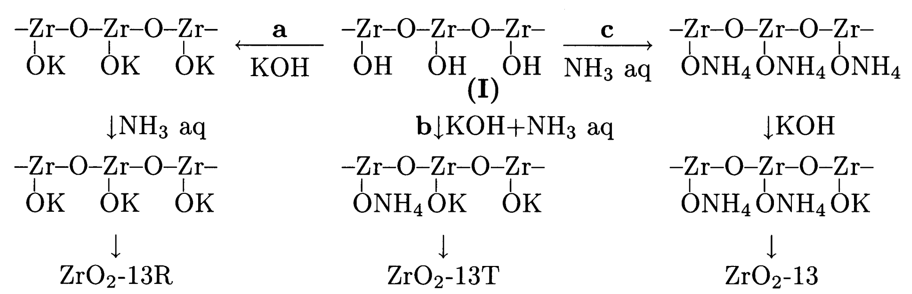


Fig. 2. Methane conversion on ZrO_2 treated at different pH. Reaction conditions: CH_4 8.5 ml min^{-1} and O_2 1.2 ml min^{-1} diluted with He. Total flow rate: 30 ml min^{-1}. Weight of catalyst: 1.4 g. Reaction temperature: 775 °C. Symbols: A, 0.5 h on-stream. B, 6 h on-stream.

tity of surface potassium.

Effect of the Sequence of the Addition of NH_3 aq and KOH Solutions on Methane Coupling. In order to separate the effect of introducing of a small quantity of potassium from the influence of surface hydroxyl groups on the improvement of C_2 selectivity over ZrO_2 with KOH treatment, three kinds of ZrO_2 were prepared. Although these catalysts were prepared with similar quantities of NH_3 aq and KOH solutions, the sequence of the addition of each alkali was different. If the influence of the surface hydroxyl groups is a principal factor regarding the increase in the C_2 selectivity, each catalyst, (ZrO_2-13, ZrO_2-13R, and ZrO_2-13T) would be expected to show similar activities in the coupling process. However, the selectivities were significantly influenced by the sequence of the addition of NH_3 aq and KOH solutions, and the methane conversions remained virtually unaffected (Fig. 3). It therefore appears that the improvement in the C_2 selectivities on ZrO_2 may be primarily attributed to the presence of small quantities of potassium, rather than the surface hydroxyl groups. It is of interest to note that the C_2 selectivity on each ZrO_2, especially on ZrO_2-13 and ZrO_2-13R, appears to be inversely related to the K/Zr ratio estimated by XPS (Table 1). Thus, the presence of excess potassium on the catalyst surface may decrease the selectivity. The amount of ion-exchanged potassium may be influenced by the relative affinities of K^+ and NH_4^+ for ion-exchange during the preparation as Scheme 1.

In the preparation of ZrO_2-13R (Scheme 1, route **a**), hydrous zirconium oxide (**I**) is ion-exchanged by KOH in a first step; since the incorporated K^+ may not be replaced by NH_4^+, ZrO_2 containing an excess of K species is produced. The content of the K species on ZrO_2-13T is expected to be less than that found with ZrO_2-13R, due to a competitive ion-exchange of NH_4^+ and K^+ to give ZrO_2-13R containing the smallest quantity of the K species (route **b**). In the standard preparation in the present work (route **c**), the amount of the K species may be influenced by the replacement of ion-exchanged NH_4^+ by K^+ to give ZrO_2-13 containing the smallest quantity of the K species. Therefore, ZrO_2 catalysts containing different amounts of ion-exchanged K species can be



Scheme 1.

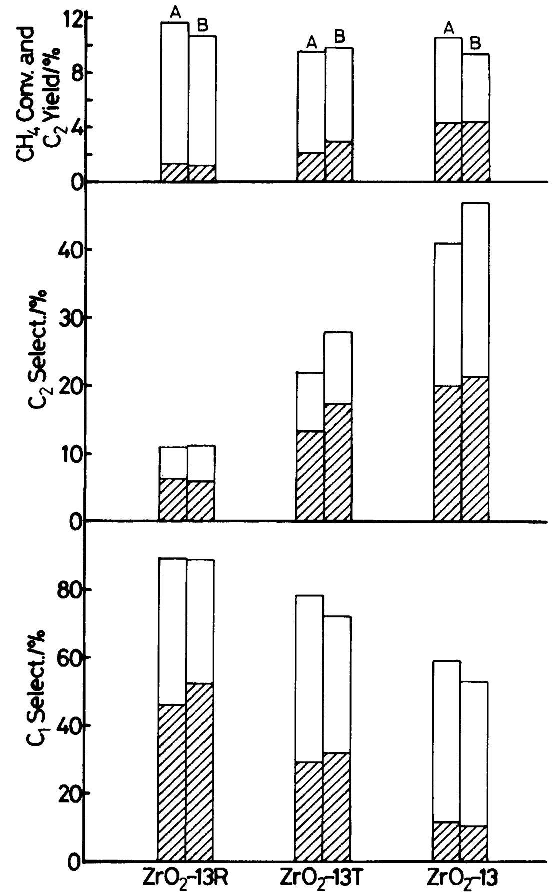


Fig. 3. Effect of the sequence of the addition of alkali solutions on the methane conversion on ZrO_2. Reaction conditons and symbols: as in Fig. 2.

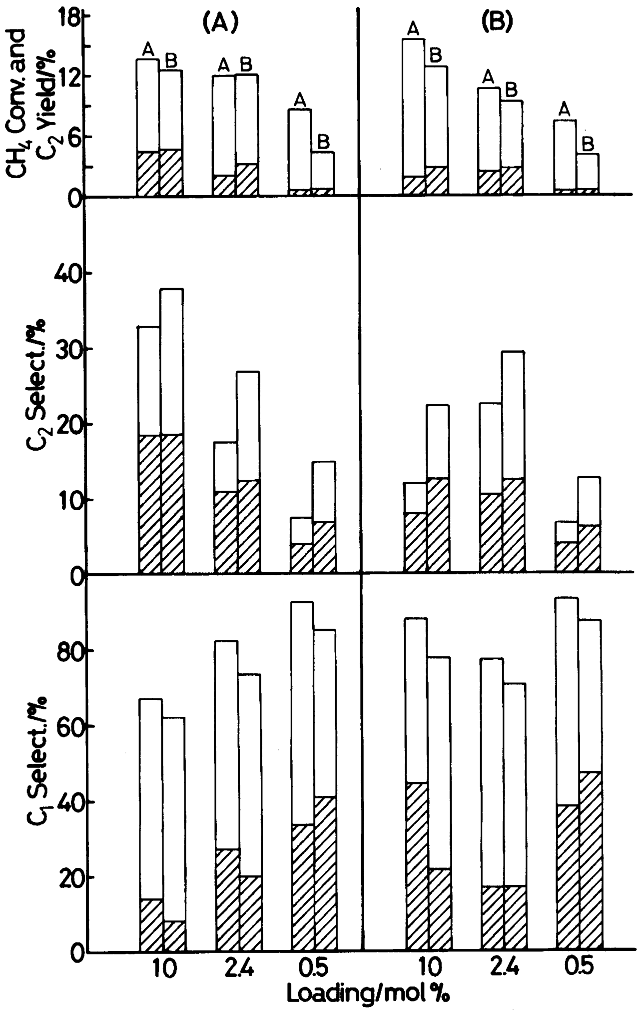


Fig. 4. Comparison of the activities for methane conversion on K_2CO_3/ZrO_2 (A) and KOH/ZrO_2 (B). Reaction conditions and symbols: as in Fig. 2.

prepared only by changing the order of the addition of KOH and NH_3 aq solutions.

In the present preparation procedure using the ion-exchange character of hydrous zirconium oxide, potassium may be well-dispersed on ZrO_2. It has sometimes been reported that a catalyst with well-dispersed cations enhances the selectivity to C_2 hydrocarbons[19,20) and, in some cases, possesses a proper basicity for the coupling reaction.[20) Therefore, the contribution of well-dispersed potassium on ZrO_2 appears to be important for improving the catalytic activity.

Comparison of the Reaction Behavior on K_2CO_3/ZrO_2 and KOH/ZrO_2. As pointed out in our previous paper,[7) the chemical nature of the ion-exchanged catalyst may be sufficiently different from that of the deposited catalyst to produce different observations concerning the methane coupling reaction on each catalyst. Although the natures of K_2CO_3 and KOH are quite different, the selectivities to C_2 compounds on K_2CO_3/ZrO_2 monotonously decreased with decreases in the loading of K_2CO_3, while those on KOH/ZrO_2 showed a maximum at a loading of 2.4% KOH (Fig. 4).

It is expected that two kinds of potassium species are present on KOH/ZrO_2, in contrast with K_2CO_3/ZrO_2. On KOH/ZrO_2, the surface of ZrO_2 is covered with ion-exchanged potassium species, and an excess of KOH is deposited over the ion-exchanged surface. Therefore, the methane conversion at the loading of 10% on KOH/ZrO_2 was relatively high (15.5%) with a high C_1 selectivity, which showed the character of a strong base of deposited KOH. With a decrease in the loading to 2.4%, the basicity of the catalyst surface would decrease and the character of ion-exchanged potassium would reflect the reaction behaviors to show a maximum C_2 selectivity. A further decrease in the loading of KOH to 0.5% leads to a reduction of the ion-exchanged potassium on the surface, as well as a decrease in the C_2 selectivity. Since only one active species of K_2CO_3 might be present on K_2CO_3/ZrO_2, the methane conversions and C_2 selectivities on K_2CO_3/ZrO_2 decrease with decreasing loading.

In conclusion, the improvement in the C_2 selectivity on ZrO_2 treated by KOH appears to be related to the ion-exchanged properties of the potassium cation. Zirconia containing a trace amount of ion-exchanged K species showed a relatively high selectivity to C_2 compounds up to 40%, compared with that found on 10% K_2CO_3/ZrO_2.

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