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Comparison of the Oxidative Coupling Reactions of Benzene with Those of Methane of Rare Earth Oxide Catalysts

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The oxidative coupling of benzene has been compared with that of methane on La_2O_3, CeO_2, Pr_6O_{11}, and Sm_2O_3. At temperatures greater than 1048 K, the gas phase oxidative coupling of benzene appears to be predominant, while the oxidation occurs catalytically at 873 K. The conversion of benzene and of methane at 873 K follows the order of $Sm_2O_3 > La_2O_3 > Pr_6O_{11} > CeO_2$, suggesting that the abstraction of hydrogen from the aromatic and the saturated compounds depends primarily on the nature of the catalyst but not the reactant. Ancillary information has also been obtained from the results of XPS analyses of both fresh catalysts and those previously used in one of the reactions.

The possibility of converting methane into value added products has occupied the attention of researchers in catalysis for a number of years.[1—4] Although much of this work has focused on partial oxidation and oxidative coupling, more recently the oxidative methylation of toluene with methane has been reported as a new method of synthesizing ethylbenzene and styrene and, additionally, of utilizing methane.[5—12] In these studies, evidence for the self-coupling of aromatic rings, and in particular benzene, was reported but with little or no elaboration, although the thermal dehydrogenation of benzene to biphenyl is a well-known industrial process.[13] Recently Yamaguchi and co-workers have reported that benzene converts to biphenyl at selectivities greater than 94% over a wide range of conversions (3—77%) of benzene; they used a temperature diffusion reactor at reaction temperatures between 1223 and 1423 K.[14] Thus the oxidative coupling of benzene to form biphenyl would be expected to occur under catalytic reaction conditions similar to those employed in the oxidative cross-coupling of toluene with methane, that is, at temperatures in the range of 823—1023 K.[5—12] Further, the thermal dehydrogenation of methane at 1473 K produced a selectivity to C_2 compounds of 94.9% at a methane conversion of 9.4%[15] while the oxidative coupling of methane on Sm_2O_3 at 973 K generated a selectivity of 85.9% at a methane conversion of 5.4%.[16]

In the present study, both oxidative coupling of benzene and of methane on La_2O_3, CeO_2, Pr_6O_{11}, and Sm_2O_3 at reaction temperatures between 873 and 1123 K have been investigated to provide comparisons of the hydrogen abstraction from aromatic and saturated compounds on each catalyst. Extensive catalytic studies on the oxidative coupling of methane over these catalysts have already been reported.[16—18] The present work also reports the results of X-ray photoelectron analyses of the catalysts subsequent to their use in the coupling process.

Experimental

Reagents La_2O_3 (99.5%), CeO_2 (99.9%), Pr_6O_{11} (99.9%), and Sm_2O_3 (99.5%) were purchased from Wako Pure Chemicals and used as received. All catalysts were pressed, crushed, and sieved to the particle size of 10—20 mesh. BET surface areas and the apparent densities of La_2O_3, CeO_2, Pr_6O_{11}, and Sm_2O_3 were 1.9 and 1.81, 18.0 and 2.29, 3.1 and 2.13, and 4.6 $m^2\,g^{-1}$ and 1.39 $g\,cm^{-3}$, respectively.

The catalytic experiments were performed in a fixed-bed continuous flow quartz reactor at atmospheric pressure.[19] The catalyst (usually 0.3 g) was initially heated at 1048 K in a continuous flow of helium, followed by a 12.5 $ml\,min^{-1}$ flow of oxygen for 1 h at the same temperature. The reactant stream consisted of CH_4 or C_6H_6 (10.7 kPa) and O_2 (2.7 kPa unless otherwise indicated) diluted with helium. Benzene was supplied to the reactor from a micro-feeder (type JP-S, Furue Science). Experiments in the absence of a catalyst were also performed under conditions similar to those employed when the catalyst was present.

The gaseous reactants and products were analyzed with an on-line Shimadzu GC-8APT gas chromatograph with a TC detector and integrator (Shimadzu C-R6A). The aromatic components such as C_6H_6, biphenyl ($C_{12}H_{10}$) and *o*-terphenyl ($C_{18}H_{14}$) were trapped with toluene at 273 K and analyzed with a Hitachi 163 gas chromatograph with an FI detector and integrator (System Instruments Co., Chromatocorder 11). Column packings used were: Molecular Sieve 5A (1.5 m×3 mm) for O_2, CH_4, and CO (318 K), Porapak N (6 m×3 mm) for CO_2, C_2H_6, C_2H_4 (363 K) and C_3 species (423 K), and 15% Apiezon Grease L/Uniport B (1 m×3 mm) for C_6H_6, toluene (383 K), $C_{12}H_{10}$ and $C_{18}H_{14}$ (543 K). The conversion of CH_4 or C_6H_6 was calculated based on the products and CH_4 or C_6H_6 introduced in the feed. The selectivities were calculated based on the conversion of CH_4 or C_6H_6 to each product on a carbon base.

X-Ray photoelectron spectra were measured by a Shimadzu ESCA-1000AX and the observed binding energies were calibrated with 285.0 eV for C 1s electron. The sample was mounted on a sample holder in air and set into the spectrometer. After measurement of the surface, argon-ion etching of the sample was carried out (2 kV, 1 min)

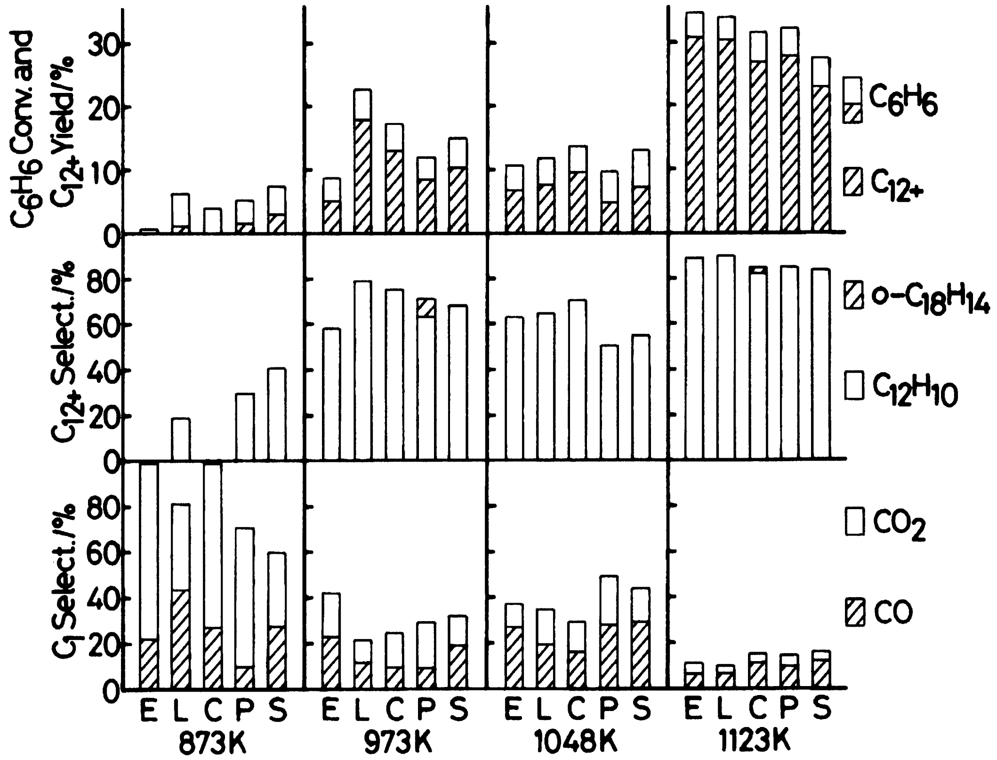

Fig. 1. The effects of temperature on the oxidative coupling of benzene. Symbols: E; Empty reactor. L; La_2O_3. C; CeO_2. P; Pr_6O_{11}. S; Sm_2O_3. Reaction conditions: Reactant; benzene=10.7 kPa and O_2=2.7 kPa diluted with He. Total flow rate=30 ml min^{-1}. Weight of catalyst=0.3 g.

and the spectra were measured again. The reference minimum argon-sputtering rate for SiO_2, Al_2O_3, and MgF_2 was 2 nm min^{-1}. In the present study, the atomic sensitivity factors of each rare earth element relative to oxygen was determined by comparison of the composition of each oxide with the area of each element in XPS after 15 s etching of each fresh calcined (773 K, 2 h) oxide. These factors were found to be 4.61, 7.39, 9.51, and 1.16 for La $3d_{5/2}$/O 1s, Ce $3d_{5/2}$/O 1s, Pr $3d_{5/2}$/O 1s, and Sm $3d_{5/2}$/O 1s, respectively.

Results and Discussion

Comparison of the Oxidative Coupling of Benzene with That of Methane. The results from the oxidative coupling of benzene on each of the rare earth oxide catalysts at 873—1123 K are shown in Fig. 1, together with those in the absence of a catalyst. The conversion of oxygen on each catalyst was almost 100%. Since, at a reaction temperature of 1123 K, the conversion of benzene and the selectivities to each product in the absence of the catalyst are similar to those in the presence of the catalyst, the homogeneous reaction of benzene contributes significantly to the process at this temperature. In contrast, at 973 K, the conversion of benzene on each catalyst was higher than that in the absence of the catalyst. At 878 K, the contribution of the homogeneous reaction was insignificant.

In the oxidative coupling of methane, the gas phase reaction at 873 and 1048 K contributes relatively little to the process in the presence of the catalyst (Fig. 2). At 873 K, the conversions of benzene and of methane with the four catalysts followed the same order: $Sm_2O_3 > La_2O_3 > Pr_6O_{11} > CeO_2$, although the values obtained for the conversion with the former reactant were considerably smaller than those found with methane. The abstraction of hydrogen from benzene and from methane, leading presumably to the formation of phenyl and methyl radicals, respectively, is dependent on the nature of the catalyst but not on that of the reactants. However, the selectivities to biphenyl and C_2 compounds increased in the order: $Sm_2O_3 > Pr_6O_{11} > La_2O_3 > CeO_2$ and $La_2O_3 > Sm_2O_3 > Pr_6O_{11} \cong CeO_2 \cong 0$, respectively. Therefore the contribution of each catalyst to the reaction of phenyl radicals appear to be different from that of the methyl radicals. It is somewhat surprising to note that the conversions of methane on Pr_6O_{11} and on Sm_2O_3 were relatively unaltered by increase of the temperature from 873 to 1048 K, although the C_2 selectivities were noticably decreased. Although it is not possible to provide a definitive explanation for these observations from the present results, the absence of temperature effects on the conversion may be related to disadvantageous changes in the surface composition.

The Effect of C_6H_6/O_2 Ratio and W/F on the Reaction of Benzene over Sm_2O_3 at 873 K. Since the reaction behavior of the oxidative coupling of benzene on a catalyst at reaction conditions similar to those used for the oxidative coupling of methane has not been reported, the oxidative coupling of benzene on Sm_2O_3

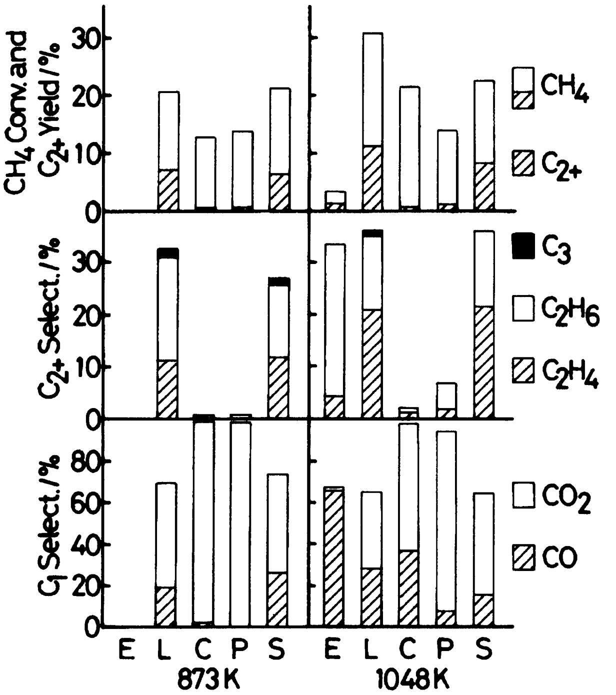

Fig. 2. The oxidative coupling of methane at 1048 and 873 K. Symbols: same as in Fig. 1. Reaction conditions: same as in Fig. 1 except the partial pressure of methane (10.7 kPa).

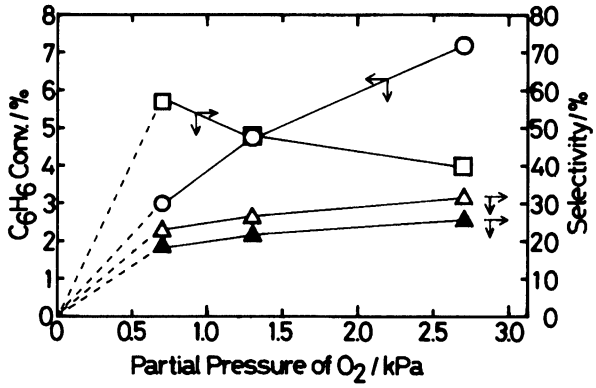

Fig. 3. The effect of partial pressure of oxygen on the oxidative coupling of benzene on Sm_2O_3 at 873 K. Reaction conditions: same as Fig. 2 except the partial pressure of O_2. Symbols: ○ C_6H_6 conversion. □ $C_{12}H_{10}$ selectivity. △ CO_2 selectivity. ▲ CO selectivity.

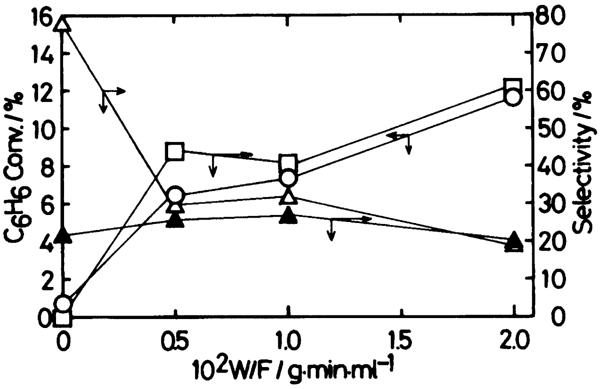

Fig. 4. The effect of W/F on the oxidative coupling of benzene on Sm_2O_3 at 873 K. Reaction conditions: same as Fig. 2 except the weight of catalyst (W). $W=0$ g at $W/F=0$, $W=0.15$ g at $W/F=0.5\times10^{-2}$, $W=0.3$ g at $W/F=1.0\times10^{-2}$ and $W=0.6$ g at $W/F=2.0\times10^{-2}$. Symbols: same as Fig. 3.

at 873 K was examined further. As expected from the results of oxidative coupling of methane on lanthanum catalysts,[18,20] the conversion of benzene and the selectivities to C_1 compounds decreased with decrease in the partial pressure of oxygen and finally benzene was completely recovered when oxygen was not supplied into the reactant stream (Fig. 3). If a lattice oxygen participates in the oxidative dehydrogenative coupling of benzene, it would be expected that the coupling reaction proceeds to some extent even in the absence of oxygen, as shown in the oxidative dehydrogenation of ethyl lactate to the pyruvate on TeO_2–MoO_3 in gas-phase.[21] Therefore, the present results in the absence of oxygen show that an active oxygen species is not a lattice oxygen species but an adsorbed oxygen species, as suggested by Lunsford and his co-workers for the oxidative coupling of methane on La_2O_3.[22] In contrast, the effects of W/F on the oxidative coupling of benzene were quite different to those in the coupling of methane (Fig. 4). The conversion of benzene decreased to 0.65% as W/F approached zero and the selectivity to the coupling product increased with increasing W/F. In contrast, it has been observed in the oxidative coupling of methane on a variety of catalysts that the conversion of methane increases with increasing W/F, while the selectivity to the coupling product decreases.[20,23,24] It is generally known that biphenyl, the coupling product in the oxidative coupling of benzene, is less active than benzene[13] while ethane is more reactive than methane, and consequently the latter coupling product is more susceptible to thermal degradation than the former at temperatures above 800 K.[25] Thus, not surprisingly, the selectivities display opposing tendencies in the two oxidative coupling processes with changes in residence time.

XPS Analyses of the Catalysts Used at 873 K. In order to obtain information on the surface of the catalysts, those previously used for a reaction at 873 K were selected for XPS analyses, since relatively little contribution of the gas-phase reaction of benzene or methane was observed at this reaction temperature.

The results of XPS analyses of La_2O_3 previously employed in the oxidative coupling of benzene or of methane and of fresh calcined oxide are described in Table 1. Two major peaks in the spectrum of C 1s on the surface were initially evident, but these vanished after argon ion-etching for 1 min. Since the binding energy of C 1s for carbon atoms bonded to oxygen is higher than 285.0 eV,[27] the peak detected at 285.0 eV can

Table 1. Binding Energies and La/O Ratios of the Fresh and Used La_2O_3 Catalysts

Reactant[a)]	Time[b)]	C 1s	O 1s	La $3d_{5/2}$	La/O
	min	eV	eV	eV	
Fresh	0	289.7, 285.0	531.8, 529.0 (2.0:1.0)[c)]	838.9, 834.8 (1.0:1.1)[c)]	0.45
	1	— —	532.7, 530.1 (1.0:1.7)[c)]	839.7, 835.1 (1.0:1.2)[c)]	0.69
Benzene	0	289.9, 285.0	532.0, 529.3 (2.4:1.0)[c)]	839.0, 835.2 (1.0:1.2)[c)]	0.39
	1	— —	532.6, 530.1 (1.0:1.2)[c)]	839.6, 836.6 (1.0:1.0)[c)]	0.58
Methane	0	289.5, 285.0	531.6, 528.9 (2.8:1.0)[c)]	838.8, 835.0 (1.0:1.3)[c)]	0.40
	1	— —	532.2, 530.0 (1.0:1.1)[c)]	839.5, 835.1 (1.0:1.2)[c)]	0.59
Ref.[26)]				834.8	0.67

a) Benzene or methane refer to the reaction (873 K) for which the catalyst was previously used. b) Etching time. c) Ratio of intensities.

Table 2. O 1s Binding Energies of Various Oxygen Species

C 1s/eV[a)]	Binding energy/eV
O^{2-} Unknown	529.7[28)]
284.6	528.8—529.0,[29)] 528.4—528.6[30)]
285.0	528.9,[31)] 529[32)]
O^- Unknown	531.2[28)]
284.6	531.5[33)]
$O_2{}^{2-}$ Unknown	532.7[28)]
284.6	532.4—533.0,[29)] 531.0—530.3[30)]
285.0	531.5[31)]
$O_2{}^-$ 284.6	532.8—533.2[29)]
$CO_3{}^{2-}$ 284.6	531.6[30)]
285.0	532[32)]
$HCO_3{}^-$ 284.6	534.1[30)]
285.0	534[32)]
$CO_4{}^{2-}$ 284.6	532.8—533.2[29)]

a) Binding energy of contaminant carbon.

be attributed to a contaminant of the sample.[26)] The peak at ca. 289.7 eV may be attributed to carbonate or carbon dioxide strongly adsorbed on the surface of the catalyst.[27)] In the O 1s spectrum, peaks at ca. 532 and 529.5 eV were observed. After the argon ion-etching, the main peak shifted from 532 to 529.5 eV, regardless of the reaction in which the catalyst had been previously used. The peak at 529.5 eV can be attributed to lattice oxygen (O^{2-}), while the peak at 532 eV cannot be identified, due to the overlap of various kinds of oxygen species between 531 and 534 eV in the O 1s spectrum (Table 2).[28—33)] Two peaks, whose intensities are not altered by ion-etching, at ca. 835 and 839 eV in the La $3d_{5/2}$ spectrum, are attributed to La^{3+} and a more oxidized La species, respectively. The surface atomic ratio (La/O) on both the fresh and the used catalysts is smaller prior to the argon ion-etching, indicating that adsorbed oxygen species are present on the surface. The ratios found with the used catalyst are relatively smaller than those in the fresh oxide with or without ion-etching, suggesting that oxygen in the bulk phase diffuses to the catalyst surface during the oxidation process. It is of interest to note that the effect of ion-etching on O 1s, La $3d_{5/2}$ and the atomic ratio of La/O showed little or no dependence on the reactant employed in the oxidation reaction.

It is worthwhile to mention a relationship between some oxygen species in Table 2 and an active species suggested in the oxidative coupling of methane.[3)] The O^- species has been suggested to be an active species on alkali/alkaline earth oxide catalysts.[34)] The peroxide ions ($O_2{}^{2-}$) have been indicated to be active species on Na_2O_2, BaO_2, and SrO_2[35)] while the superoxide ions ($O_2{}^-$) did not activate methane.[35)] However the $O_2{}^-$ species have been detected by EPR on active catalysts such as the rare earth oxides. In this case, an equilibrium between the superoxide ions and the peroxide ions has been proposed.[36)]

The XPS spectra for CeO_2 displayed a broad signal, which was resolved with a curve fitting technique, for Ce $3d_{5/2}$ (Table 3). Of the two peaks in the O 1s spectrum, that at ca. 529.5 eV can be attributed to the lattice oxygen. The intensity of this peak decreased after use of the catalyst in either of the reactions and the Ce/O atomic ratio in the catalyst previously used with methane was approximately one-half that used with benzene. These results may suggest that the interaction of gas-phase oxygen and the oxide together with mobility of oxygen species in the oxide are strongly influenced by the reactants.

In the case of Pr_6O_{11} (Table 4), O 1s peaks at ca. 532 and 529.5 eV are observed with the fresh catalyst and the catalyst used for the oxidative coupling of benzene, while three peaks appeared in the spectrum of O 1s for

Table 3. Binding Energies and Ce/O Ratios of the Fresh and Used CeO_2 Catalysts

Reactant$^{a)}$	Time$^{b)}$	C 1s	O 1s	Ce $3d_{5/2}$	Ce/O
	min	eV	eV	eV	
Fresh	0	289.6, 285.0	531.7, 529.7 (1.0:3.7)$^{c)}$	889.3, 885.7, 883.1 (2.4:1.0:3.1)$^{c)}$	0.40
	1	— —	532.5, 530.4 (1.0:3.2)$^{c)}$	890.1, 886.8, 883.4 (1.0:3.3:3.7)$^{c)}$	0.50
Benzene	0	288.6, 285.0	531.8, 529.6 (1.0:1.4)$^{c)}$	889.7, 886.3, 882.9 (2.3:1.0:2.8)$^{c)}$	0.27
	1	— —	532.0, 529.7 (1.0:1.7)$^{c)}$	889.6, 886.1, 883.1 (1.0:3.3:4.0)$^{c)}$	0.42
Methane	0	— 285.0	532.4, 529.7 (1.0:1.4)$^{c)}$	888.9, 885.7, 883.0 (5.7:1.0:7.9)$^{c)}$	0.12
	1	— —	532.0, 529.9 (1.0:1.8)$^{c)}$	889.2, 885.9, 883.0 (1.0:2.2:3.1)$^{c)}$	0.24
Ref.$^{26)}$				881.9	0.50

a) Benzene or methane refer to the reaction (873 K) for which the catalyst was previously used. b) Etching time. c) Ratio of intensities.

Table 4. Binding Energies and Pr/O Ratios of the Fresh and the Used Pr_6O_{11} Catalysts

Reactant$^{a)}$	Time$^{b)}$	C 1s	O 1s	Pr $3d_{5/2}$	Pr/O
	min	eV	eV	eV	
Fresh	0	289.8, 285.0	— 531.7, 529.0 (1.4:1.0)$^{c)}$	933.1, 928.1 (3.7:1.0)$^{c)}$	0.33
	1	— —	— 531.6, 529.5 (1.0:2.2)$^{c)}$	933.2, 928.1 (3.0:1.0)$^{c)}$	0.60
Benzene	0	289.7, 285.0	— 531.8, 529.2 (10.6:1.0)$^{c)}$	934.3, 929.5 (5.4:1.0)$^{c)}$	0.19
	1	— —	— 531.9, 529.7 (1.0:1.3)$^{c)}$	934.0, 929.0 (2.6:1.0)$^{c)}$	0.52
Methane	0	289.7, 285.0	534.4, 532.0, 529.1 (1.0:7.2:2.8)$^{c)}$	934.0, 929.1 (4.2:1.0)$^{c)}$	0.31
	1	— —	533.6, 531.7, 529.3 (1.0:9.3:18.6)$^{c)}$	933.4, 928.5 (2.8:1.0)$^{c)}$	0.58
Ref.					0.55

a) Benzene or methane refer to the reaction (873 K) for which the catalyst was previously used. b) Etching time. c) Ratio of intensities.

the catalyst used in the methane oxidation. Two peaks at ca. 533.2 and 531.2 eV which have previously been observed in fresh Pr_6O_{11} catalyst were attributed to the adsorbed species of oxygen and the lattice oxygen, respectively.[27] In the present study, a similar conclusion is less evident. However, the dramatic change of the ratio of intensity for O 1s species and similar behavior of Pr/O after the ion-etching of each catalyst used suggest that the change of charge of oxygen species on and in Pr_6O_{11} is strongly dependent on each substrate: benzene or methane. In contrast, the changes of the ratio of intensity for Pr $3d_{5/2}$, which are observed at ca. 933.5 and 929 eV, and the change of Pr/O produced by the ion-etching are little influenced by the reactants.

In the spectrum of Sm_2O_3, two oxygen species were observed at ca. 532 and 529 eV and one samarium species (Sm^{3+}) at ca. 1083.5 eV, together with two carbon species on the surface, as described in Table 5. After the argon ion-etching, the peak at 529 eV, which can be attributed to the lattice oxygen, was increased in both the used and the fresh catalysts. It is of interest to note that the quantities of oxygen species on the surface and after the etching in each catalyst used are smaller than those in the fresh catalyst as estimated from Sm/O ratio. Therefore it appears that the oxygen species in Sm_2O_3 are abstracted during the oxidative coupling reactions and the abstraction is more pronounced when benzene is used as a reactant.

The Correlation of XPS Results for Oxygen Species with the Reaction Behaviors at 873 K. Although it is difficult to identify an active species on each rare earth oxide catalyst using the present XPS results, it is of interest to point out some relationships between oxygen species on each catalyst and the reaction behaviors. Over La_2O_3, Pr_6O_{11}, and Sm_2O_3, the ratio of the intensity of one peak at ca. 532 eV in the O 1s

Table 5. Binding Energies and Sm/O Ratios of the Fresh and Used Sm_2O_3 Catalysts

Reactant[a)]	Time[b)]	C 1s	O 1s	Sm $3d_{5/2}$	Sm/O
	min	eV	eV	eV	
Fresh	0	289.9, 285.0	531.9, 529.4 (2.2:1.0)[c)]	1084.0	0.41
	1	— —	533.1, 530.7 (1.0:1.9)[c)]	1084.9	0.69
Benzene	0	289.8, 285.0	531.5, 528.9 (4.3:1.0)[c)]	1083.6	1.50
	1	— —	532.8, 530.2 (1.0:1.0)[c)]	1084.4	2.61
Methane	0	288.6, 285.0	531.3, 528.6 (3.1:1.0)[c)]	1082.9	0.65
	1	— —	532.5, 529.8 (1.4:1.0)[c)]	1083.6	1.04
Ref.[26)]				1084.3	0.67

a) Benzene or methane refer to the reaction (873 K) for which the catalyst was previously used. b) Etching time. c) Ratio of intensities.

spectrum to another peak at ca. 529 eV (lattice oxygen) was decreased after the ion-etching, while the intensity at ca. 529 eV was larger than that at ca. 532 eV, regardless of the etching on CeO_2. The former three catalysts revealed relative high selectivity to the corresponding coupling products, except for the coupling reaction of methane on Pr_6O_{11}, but the deep oxidation to CO and CO_2 exclusively proceeded on the latter CeO_2. Since it has been suggested that an active oxygen species on the rare earth oxides are adsorbed forms of oxygen[3)] it appears that the active adsorbed oxygen species are included in the O 1s signal at ca. 532 eV. On Pr_6O_{11}, the contribution of other oxygen species at 534 eV which were detected only after the methane coupling reaction on the oxide, appears to affect an active oxygen species to decrease the selectivity to C_2 compounds. The CeO_2 catalyst is generally known to be an oxygen reservoir and it may be expected that the nature of the adsorbed oxygen species will be quite different to that on other rare earth oxides, as revealed in the present XPS results.

Conclusion

It is difficult to correlate the present XPS results with the reaction behavior of oxidative coupling of benzene or methane systematically. However it is evident that the results obtained from the coupling reactions of benzene and of methane show a strong dependence on the nature of the catalyst, but relatively little on the reactant itself. The oxidative coupling of benzene is a significant contributor to reactions, in which aromatic compounds are oxidatively dehydrogenated under reaction conditions similar to those employed in the oxidative coupling of methane.

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