

Temperature-Programmed Reduction and XRD Studies of the Interactions in Supported Rhodium Catalysts and Their Effect on Partial Oxidation of Methane to Synthesis Gas

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In the present paper, comprehensive temperature-programmed reduction and X-ray diffraction studies were conducted, with particular emphasis on the effect of calcination temperature on the interactions between rhodium oxide and support. The formation of a compound between rhodium and support oxide is strongly dependent on the nature of the support and the calcination temperature. No such compounds were formed over γ -Al₂O₃ and SiO₂ supported Rh catalysts even after a calcination at a temperature as high as 950°C. However, LaRhO₃, MgRh₂O₄, YRhO₃, and RhTaO₄ could be formed over La₂O₃, MgO, Y₂O₃, and Ta₂O₅ supported catalysts after their calcination at suitable temperatures. The ease of formation of these compounds decreased in the sequence MgO > La₂O₃ >> Y₂O₃ > Ta₂O₅. The lower reducibilities of these compounds compared to that of Rh₂O₃ brought evidence of increased Rh–O bond strength. In other words, the formation of these compounds after calcination is an indication of strong interactions between rhodium and support. At a reaction temperature of 750°C, La₂O₃ and MgO provided stable catalytic activities and selectivities during 100 h of reaction, whereas deactivation was observed over the Y₂O₃ and Ta₂O₅ supported catalysts. However, because compounds between the latter two supports and Rh₂O₃ could be formed at higher temperatures, reactions at higher temperatures have also been carried out. It was found that the stability of the 1 wt% Rh/Ta₂O₅ could be notably improved at a reaction temperature of 900°C, and that the stability of the 1 wt% Rh/Y₂O₃ could be improved at a reaction temperature of 850°C. © 2000 Academic Press

Key Words: methane partial oxidation; syngas; Rh catalyst; TPR; XRD.

1. INTRODUCTION

The background of the present work and the relevant references were given in a previous paper (1). In that paper, the effect of the nature of the support on the performance of Rh-based catalysts in the partial oxidation of methane to synthesis gas was investigated. It was found that, with the exception of Ta₂O₅, the reducible oxide supports provided much lower methane conversions and selectivities to CO and H₂ than the irreducible ones. Among the irreducible

metal oxides, γ -Al₂O₃, La₂O₃, and MgO provided stable catalytic activities and selectivities during 100 h of reaction at a furnace temperature of 750°C, while deactivation occurred over SiO₂ and Y₂O₃. The reducible Ta₂O₅ provided activity, selectivities, and deactivation comparable to those of the irreducible Y₂O₃. It was suggested that the strong interactions between rhodium and magnesium or lanthanum oxides (especially the formation of MgRh₂O₄ or LaRhO₃) were responsible for the high stability of MgO and La₂O₃ supported Rh catalysts. No such compounds were detected for Y₂O₃ and Ta₂O₅ at a calcination temperature of 800°C. An alternate sintering–redispersion mechanism was proposed to explain the high stability of γ -Al₂O₃ supported catalyst for which no compound between Al₂O₃ and Rh₂O₃ could be identified.

In the work described in present paper, comprehensive temperature-programmed reduction (TPR) and X-ray diffraction (XRD) studies were conducted, with the emphasis on the effect of calcination temperature. It was found that not only MgO and La₂O₃ but also tantalum and yttrium oxides form compounds with Rh₂O₃ after calcination at suitable high temperatures. The stabilities of the latter two supported catalysts could be notably improved when the reaction was conducted at temperatures at which the compounds YRhO₃ or RhTaO₄ could be formed.

2. EXPERIMENTAL

2.1. Catalyst Preparation

The following powder supports were used: γ -Al₂O₃ and Ta₂O₅ from Alfa, and La₂O₃, MgO (obtained from MgO₂ · xMgO via calcination at 800°C for 4 h), SiO₂, and Y₂O₃ from Aldrich. The supported rhodium catalysts were prepared by impregnating the support with an ethanol solution of Rh(NO₃)₃ · 2H₂O (Alfa), followed by overnight drying at 110°C. The samples thus obtained were subjected to calcination in air at 800°C for 4 h, unless otherwise stated. The calcined catalysts will be denoted Rh(O)/M_xO_y(800°C), where the temperature inside the

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parentheses indicates the calcination temperature during catalyst preparation. The catalysts reduced in H_2 will be denoted Rh/M_xO_y . Rh loading means weight percent of Rh in the reduced catalyst.

2.2. Catalyst Testing

All activity assays were conducted under atmospheric pressure in a fixed-bed vertical quartz reactor (3 mm inside diameter) immersed in an electronically controlled furnace. Five or ten milligrams of catalyst, which was held on quartz wool, was used in each run. A thermocouple was inserted into the middle of the catalyst bed to measure the temperature of the catalyst and another was located in the gas near the exit of the catalyst bed to measure the temperature of the gaseous phase. Before the testing was performed, the catalyst was reduced. The reduction was carried out in the reactor by increasing the temperature up to $750^\circ C$ at $20^\circ C/min$ in a H_2 flow (20 ml/min). The reactants and products were analyzed with an online gas chromatograph equipped with Porapak Q and 5A molecular sieve columns. An ice-cold trap was located between the reactor exit and the GC sampling valve to remove the water formed during reaction.

Methane (99.97% purity, from Matheson) and oxygen (99.9% purity, from Cryogenic) were used without further purification. The gases were premixed ($CH_4/O_2 = 2/1$) before being introduced into the reactor.

The methane conversion and product selectivities were calculated on the basis of the carbon and hydrogen balances by neglecting any coking (some coking was observed as carbon deposition on the thermocouple downstream of the catalyst bed after a long time of reaction). The effect of the nature of the support on the conversion and product selectivities over the 1 wt% Rh catalysts was reported in a previous paper (1).

2.3. Catalyst Characterization

The surface areas after calcination and the Rh surface areas after reduction for the 1 wt% Rh catalysts were reported previously (1). Because 1 wt% Rh loading is too low for XRD analysis, 10 wt% $Rh(O)/M_xO_y$ ($M = Al, La, Mg, Si, Y,$ and Ta) samples were prepared for the XRD and TPR characterizations. The TPR results for the 10 wt% Rh catalysts calcined in an air flow at $800^\circ C$ are in agreement with those (1) of the 1 wt% Rh ones calcined in air at the same temperature.

2.3.1. Temperature-programmed reduction (TPR). The TPR profile of the catalyst was obtained by heating the sample, held on quartz wool in a quartz reactor (4 mm inside diameter) immersed in an electronically controlled furnace, from 50 to $850^\circ C$ at a rate of $20^\circ C/min$ in a flow of 2.5% H_2/Ar mixture (35 ml/min). The H_2/Ar gas mixture was purified with Hydro-Purge II and Oxy-Trap columns before use and the hydrogen consumed in TPR was determined

with a thermal conductivity detector (TCD). Twelve and one-half milligrams of sample calcined in air at $800^\circ C$ for 4 h was used in the first TPR run. To investigate the effect of calcination temperature on the TPR patterns of a sample, the sample used in the first TPR run was reoxidized in an air flow (30 ml/min) for 1 h at a new calcination temperature and then a new assay was conducted after the sample was cooled to $50^\circ C$, and so on. The calcination temperatures were in the range $600^\circ C \leq T \leq 950^\circ C$, in increasing order.

2.3.2. X-ray powder diffraction (XRD). The X-ray powder diffraction (XRD) was performed on a Siemens D500 X-ray diffractometer, using the $CuK\alpha$ radiation, at 40 kV and 30 mA.

3. RESULTS

3.1. Catalyst Characterization

The effect of calcination temperature on the TPR patterns of 10 wt% Rh/M_xO_y ($M = Al, La, Mg, Si, Y,$ and Ta) was comprehensively investigated and the results are presented in Figs. 1–6.

Two TPR peaks, one at 180 – $200^\circ C$ and the other at 350 – $400^\circ C$, were observed for the La_2O_3 supported Rh catalyst (Fig. 1). At the calcination temperature of $700^\circ C$, the

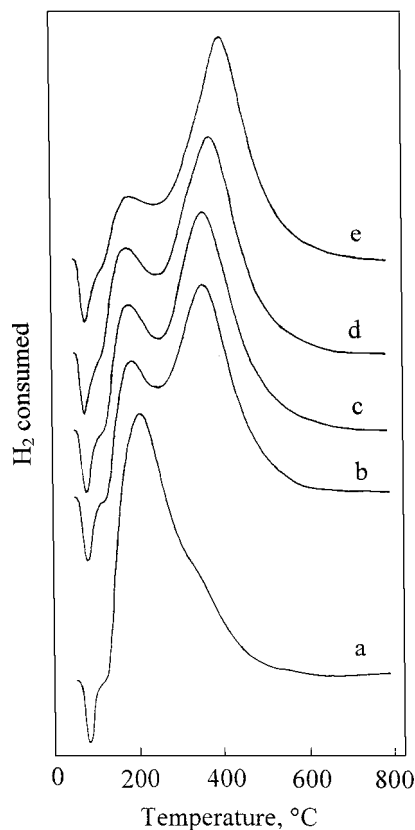


FIG. 1. TPR profiles of 10 wt% $Rh(O)/La_2O_3$ calcined in an air flow for 1 h at $700^\circ C$ (a), $800^\circ C$ (b), $850^\circ C$ (c), $900^\circ C$ (d), and $950^\circ C$ (e).

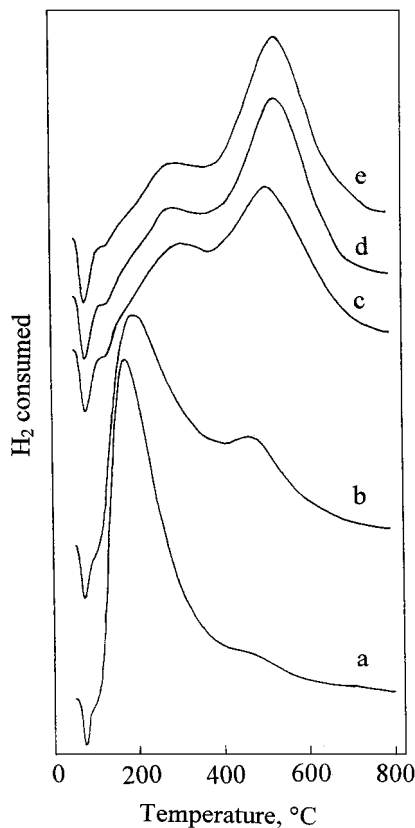


FIG. 2. TPR profiles of 10 wt% Rh(O)/MgO calcined in an air flow for 1 h at 600°C (a), 700°C (b), 800°C (c), 900°C (d), and 950°C (e).

high-temperature reduction peak (denoted HTR) appeared as a shoulder. It became, however, distinct when the calcination temperature was increased to 800°C. With the increase in the calcination temperature, the intensity of the HTR peak increased, whereas that of the low-temperature reduction peak (denoted LTR) decreased.

Similarly, two TPR peaks, at 180–300°C and at 470–530°C, were observed for the MgO supported catalyst (Fig. 2). The LTR peak shifted by about 20°C when the calcination temperature was increased from 600 to 700°C, but shifted notably from about 190°C to about 310°C when the calcination temperature was increased from 700 to 800°C. A further increase in the calcination temperature had no notable influence on the position of the LTR peak.

As shown in Fig. 3, over the Y₂O₃ supported catalyst, only one peak at about 220°C was present for a calcination temperature of 800°C. Two peaks at about 220 and 380°C, however, appeared after the catalyst was calcined at 850°C, indicating that a new compound containing Rh was formed. With the further increase of the calcination temperature to 950°C, the LTR peak almost disappeared and the HTR peak shifted to about 410°C.

As shown in Fig. 4, over the Ta₂O₅ supported catalyst, only one peak at about 180°C appeared for a calcination

temperature of 800°C. A HTR peak at about 470°C appeared, however, when the calcination temperature was increased to 850°C, and at 950°C the LTR peak almost disappeared.

For the γ -Al₂O₃ supported catalyst, only one TPR peak, at about 160–170°C, was present (Fig. 5). The intensity of the TPR peak decreased to some extent after the catalyst was calcined in an air flow at 950°C, but was restored to a level comparable to that observed in the first TPR run (in which the catalyst was calcined in air at 800°C for 4 h) after it was calcined again in an air flow at 800°C for 1 h; hence, the process was reversible.

Only one TPR peak at about 160–180°C was noted for the SiO₂ supported catalyst (Fig. 6). The intensity of the peak decreased tremendously after the catalyst was calcined in an air flow at 950°C for 1 h. However, unlike the γ -Al₂O₃ supported catalyst, no notable change in intensity occurred after the catalyst was calcined again in an air flow at 800°C; hence, the process was irreversible.

The data and the assignments of the XRD patterns of the 10 wt% Rh(O)/M_xO_y (M = Al, La, Mg, Si, Y, and Ta) catalysts are listed in Table 1. Only Rh₂O₃ was detected over the 10 wt% Rh(O)/ γ -Al₂O₃(800°C) and 10 wt% Rh(O)/SiO₂(800°C) catalysts, and this is in agreement with the

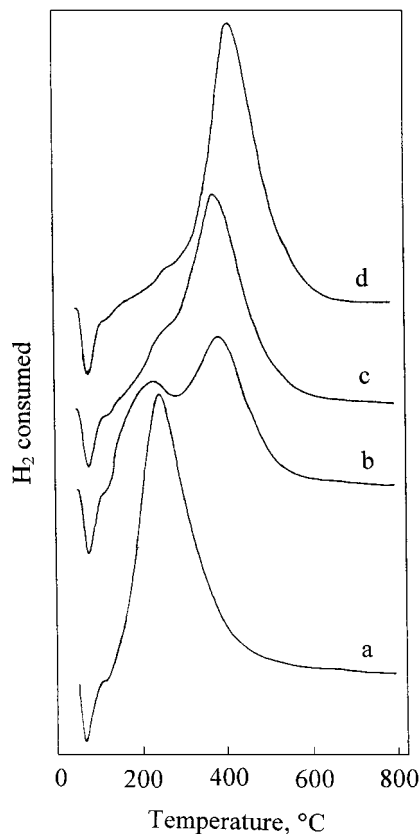


FIG. 3. TPR profiles of 10 wt% Rh(O)/Y₂O₃ calcined in an air flow for 1 h at 800°C (a), 850°C (b), 900°C (c), and 950°C (d).

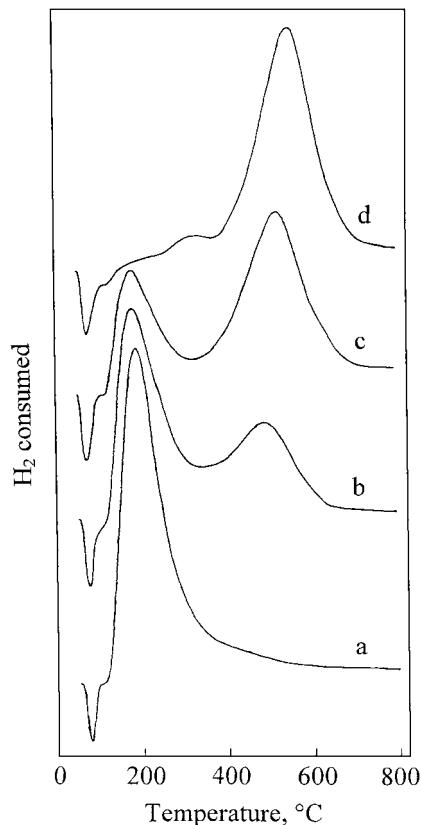


FIG. 4. TPR profiles of 10 wt% Rh(O)/Ta₂O₅ calcined in an air flow for 1 h at 800°C (a), 850°C (b), 900°C (c), and 950°C (d).

TPR results (Figs. 5 and 6). Over the 10 wt% Rh(O)/La₂O₃(800°C), besides Rh₂O₃, LaRhO₃ was also detected, and this is again in agreement with the TPR results which exhibited two TPR peaks (Fig. 1b). However, over the 10 wt% Rh/MgO(800°C), only the compound MgRh₂O₄ was detected, while two peaks were present in the TPR spectra (Fig. 2c). Over the 10 wt% Rh/Y₂O₃(800°C) and 10 wt% Rh/Ta₂O₅(800°C) catalysts, only Rh₂O₃ was identified, and this is again in agreement with the TPR spectra, which exhibited only LTR peaks (Figs. 3a and 4a). However, after the two catalysts were further calcined in air at 950°C for 2 h, only the compounds YRhO₃ and RhTaO₄ could be identified. This is again in agreement with the TPR spectra, which exhibited only HTR peaks (Figs. 3d and 4d).

3.2. Stabilities at Different Reaction Temperatures over 1 wt% Rh/Ta₂O₅ and 1 wt% Rh/Y₂O₃ Catalysts

As shown in Table 2, the stability of the 1 wt% Rh/Ta₂O₅ catalyst was notably influenced by the space velocity (SV). At SV = 720,000 ml g⁻¹ h⁻¹, the activity decreased during the first 24 h of reaction, as indicated by the values of C_{10h}/C_{1h} and C_{24h}/C_{1h} (<1), but it remained unchanged during the first 24 h of reaction at a SV of 90,000 ml g⁻¹ h⁻¹. In conclusion, the stability of the catalyst improved notably

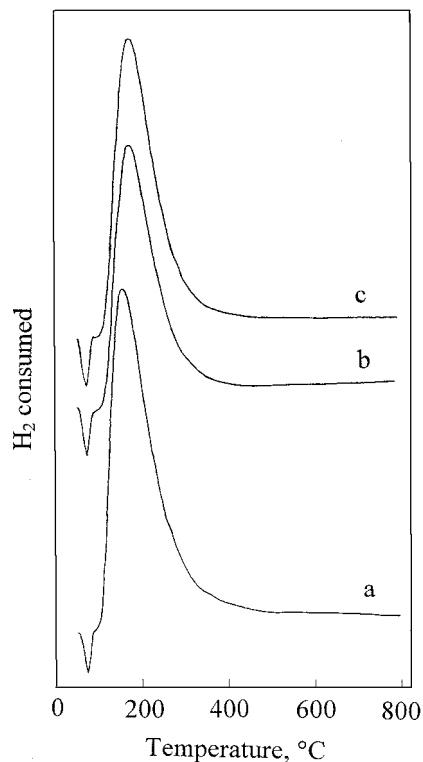


FIG. 5. TPR profiles of 10 wt% Rh(O)/ γ -Al₂O₃ calcined in air at 800°C for 4 h (a), and calcined in an air flow for 1 h at 950°C (b) and at 800°C (c).

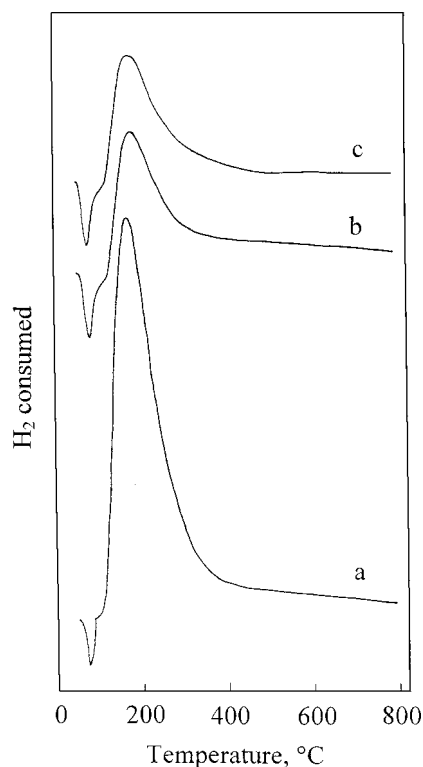


FIG. 6. TPR profiles of 10 wt% Rh(O)/SiO₂ calcined in air at 800°C for 4 h (a), and calcined in an air flow for 1 h at 950°C (b) and at 800°C (c).

TABLE 1
Data and Assignments of XRD Patterns of Calcined 10 wt% Rh(O)/M_xO_y Catalysts

Catalyst	Pretreatment	<i>d</i> (Å)	Assignments	Refs.
10 wt% Rh(O)/Al ₂ O ₃	Calcined at 800°C for 4 h	1.39, 1.96; 2.50, 2.68, 1.70	γ-Al ₂ O ₃ Rh ₂ O ₃	1
10 wt% Rh(O)/La ₂ O ₃	Calcined at 800°C for 4 h	2.93, 1.95, 3.34, 1.74, 1.64; 2.76, 3.45; 2.60, 2.79	La ₂ O ₃ LaRhO ₃ Rh ₂ O ₃ (minor)	1
10 wt% Rh(O)/MgO	Calcined at 800°C for 4 h	2.09, 1.48, 1.21, 1.27; 2.53, 4.76, 2.09, 1.48, 2.42	MgO MgRh ₂ O ₄	1, 2
10 wt% Rh(O)/SiO ₂	Calcined at 800°C for 4 h	2.52, 2.69, 1.69	Rh ₂ O ₃	2
10 wt% Rh(O)/Y ₂ O ₃	(a) Calcined at 800°C for 4 h	3.06, 1.87, 2.65, 1.60, 4.33; 2.54, 2.71, 1.72	Y ₂ O ₃ Rh ₂ O ₃	this work
	(b) Calcined at 950°C for 2 h following (a)	3.06, 1.87, 2.65, 1.60, 4.33; 2.71, 2.62, 2.85, 1.89, 3.44	Y ₂ O ₃ YRhO ₃	
10 wt% Rh(O)/Ta ₂ O ₅	(a) Calcined at 800°C for 4 h	3.13, 3.85, 2.43, 3.08, 2.41, 1.65, 1.94, 1.82; 2.52, 2.75, 1.70	Ta ₂ O ₅ Rh ₂ O ₃	this work
	(b) Calcined at 950°C for 2 h following (a)	3.13, 3.84, 2.44, 3.08, 2.41, 1.65, 1.94, 1.82; 1.65, 2.53, 3.29	Ta ₂ O ₅ RhTaO ₄	

with decreasing SV. Consequently, meaningful conclusions about the stability of a catalyst should be obtained by carrying out the reaction at a sufficiently high SV. We selected SVs $\geq 360,000$ ml g⁻¹ h⁻¹ for the stability testing. All the methane conversions reported in Table 2 are lower than the thermodynamic equilibrium data (3) at the temperatures of the catalyst bed.

As indicated by the TPR and XRD experiments, no compounds between rhodium and yttrium or tantalum oxides were formed at a calcination temperature of 800°C; YRhO₃ and RhTaO₄ were, however, generated at a calcination temperature of 850°C, and the intensities of the HTR peaks corresponding to YRhO₃ and RhTaO₄ became stronger than those of Rh₂O₃ at calcination temperatures of 850 and 900°C, respectively. Consequently, it is of interest to compare the reaction behaviors at different reaction temperatures, since the interactions between rhodium and yttrium or tantalum oxides are strongly dependent on tem-

perature. We carried out the partial oxidation reaction at furnace temperatures of 750 and 850°C over the 1 wt% Rh/Y₂O₃, and at 750 and 900°C over the 1 wt% Rh/Ta₂O₅. The catalyst temperature was recorded during the reaction and was found in all cases to be only a little higher than the furnace temperature. The deactivation is defined as $[(C^{\max} - C)/C^{\max}] \times 100$, where *C* denotes the conversion of methane and *C*^{max} the maximum conversion. After 48 h of reaction, the deactivations over the Y₂O₃ supported catalysts, calculated from Fig. 7, were 8.5% at 750°C and 4.2% at 850°C. Over the Ta₂O₅ supported catalysts, the

TABLE 2

Effect of the SV on the Deactivation Characteristics of 1 wt% Rh/Ta₂O₅

SV (ml g ⁻¹ h ⁻¹)	Reaction temp., furnace/bed (°C)	C _{1h} ^a (%)	C _t /C _{1h}		
			C _{10h} /C _{1h}	C _{24h} /C _{1h}	C _{32h} /C _{1h}
720,000	750/828	61.1	0.92	0.88	n.a. ^b
360,000	750/813	64.9	0.94	0.92	0.89
240,000	750/798	71.6	0.98	0.95	n.a.
180,000	750/794	80.4	0.99	0.99	0.98
90,000	750/780	83.6	1.01	1.00	0.99

^a C_{1h} means methane conversion after 1 h of reaction.

^b n.a. means not available.

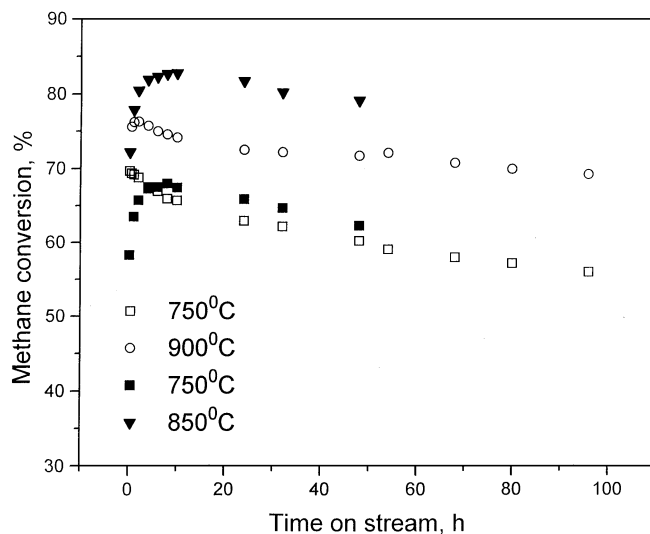


FIG. 7. Effect of time on stream on the activity of 1 wt% Rh/Y₂O₃ (solid) and 1 wt% Rh/Ta₂O₅ (open). *P* = 1 atm, CH₄/O₂ = 2.0, SV = 720,000 ml g⁻¹ h⁻¹ for the former and 360,000 ml g⁻¹ h⁻¹ for the latter.

deactivations after 96 h of reaction were 19.1% at 750°C and 9.2% at 900°C. One can conclude that the stability can be notably improved for the above two kinds of supported catalysts when suitable reaction temperatures are selected.

4. DISCUSSION

Over the 10 wt% Rh/ γ -Al₂O₃(800°C) and 10 wt% Rh/SiO₂(800°C) catalysts, only Rh₂O₃ was detected by XRD (Table 1), and only a single TPR peak (below 200°C) was observed for each of the two catalysts (Figs. 5 and 6). Because Rh₂O₃ precursor can be easily reduced (4, 5), it is reasonable to attribute the LTR peaks in Figs. 1–4 to the reduction of Rh₂O₃. The HTR peaks can be attributed to the reduction of the compound formed between the rhodium and support oxide during the calcination process. The compounds identified by XRD (Table 1) are LaRhO₃, MgRh₂O₄, YRhO₃, and RhTaO₄, respectively, for the calcined La₂O₃, MgO, Y₂O₃, and Ta₂O₅ supported catalysts. LaRhO₃ and YRhO₃ have the structure of a perovskite, MgRh₂O₄ has the structure of a spinel, and RhTaO₄ has a tetragonal structure. With the increase in calcination temperature, no significant temperature shift could be noted for the LTR peak, except for the 10 wt% Rh(O)/MgO catalyst. In the latter case, a positive shift of about 120°C, from 190 to 310°C, was observed when the calcination temperature was increased from 700 to 800°C (Fig. 2). Because only the MgRh₂O₄ phase was detected by XRD (Table 1), it is likely that either the amount of Rh₂O₃ generated or the size of the Rh₂O₃ particles was too small to be detectable by XRD.

The formation of a compound between the rhodium and support oxide is strongly dependent on the nature of the support and the calcination temperature. No compound was formed over the calcined γ -Al₂O₃ and SiO₂ supported catalysts even for calcination temperatures as high as 950°C. MgO formed most easily a compound with rhodium oxide, as revealed by the distinct HTR shoulder in the TPR spectrum of the catalyst calcined in an air flow at 700°C. For La₂O₃ and MgO supported Rh catalysts and at a calcination temperature of 800°C, the amounts of LaRhO₃ and MgRh₂O₄ were greater than those of Rh₂O₃ (as indicated by the relative intensities of the HTR and LTR peaks); no compound was formed over the Y₂O₃ and Ta₂O₅ supported catalysts calcined at 800°C. However, YRhO₃ and RhTaO₄ were formed when the calcination temperature was increased to 850°C. In conclusion, the ease of formation of these compounds decreased in the sequence MgO > La₂O₃ \gg Y₂O₃ \geq Ta₂O₅. The lower reducibilities of these compounds (LaRhO₃, MgRh₂O₄, YRhO₃, and RhTaO₄) compared to that of Rh₂O₃ are an indication for the strong interactions between rhodium and support.

In a previous paper (1), we reported that at a reaction temperature of 750°C the Rh catalysts supported on

γ -Al₂O₃, La₂O₃, and MgO and calcined at 800°C provided stable catalytic activities during 100 h of reaction. However, deactivation occurred over the SiO₂, Y₂O₃, and Ta₂O₅ supported catalysts. With the exception of γ -Al₂O₃ supported catalyst, the catalysts for which no compounds were formed after calcination exhibited a decay in activity during reaction. The strong interactions between rhodium and magnesium or lanthanum oxides were most likely responsible for the high stabilities of the MgO and La₂O₃ supported catalysts. This implies that if one could generate compounds between Rh₂O₃ and Ta₂O₅ or Y₂O₃ one could increase the stability of the corresponding supported catalysts. The TPR experiments indicated that such compounds did form if high enough calcination temperatures (>800°C) were used. We found that at a reaction temperature of 750°C the 1 wt% Rh/Ta₂O₅ catalyst calcined at 950°C and reduced by increasing the temperature to 750°C in a flow of H₂ still decayed at a rate comparable to that of the same catalyst calcined at 800°C; the deactivation after 96 h of reaction was 16.0% for the former and 19.1% for the latter. However, as shown in Fig. 7, the stability of the 1 wt% Rh/Ta₂O₅ calcined at 950°C was notably improved at a reaction temperature of 900°C. Over the 1 wt% Rh/Y₂O₃ catalyst, similar results were obtained, the stability being higher at a reaction temperature of 850°C than at 750°C.

The stability of the catalyst can be explained as follows. During reduction, metallic sites, which are responsible for the formation of the synthesis gas, are generated via the reduction of Rh₂O₃ and of the compound. Under reaction conditions, the atmosphere in the reactor is both reductive and oxidative, because of the coexistence of reductive (CH₄, CO, and H₂) and oxidative (O₂, CO₂, and H₂O) compounds. The reduced catalyst is reoxidized and a redox process occurs over the working catalyst (6–9). One could speculate that a catalyst is stable when a quasi-steady-state concentration of metallic sites is generated (the rates of reduction and oxidation become comparable). The strong interactions with the compound lessen the metal sintering and moderate the rates of the oxidation and reduction. This moderation makes the achievement of a quasi-steady state possible. Consequently, if the reaction takes place at a suitable temperature at which strong interactions between metal and support can be induced, the activity of the catalyst is expected to have a higher stability.

As shown in Fig. 6, the intensity of the TPR peak of the SiO₂ supported Rh catalyst decreased tremendously (compared to that of the TPR peak of the catalyst calcined in air at 800°C for 4 h) after the catalyst was calcined in an air flow at 950°C. This is an indication of metal sintering, because the intensity of the peak is expected to be higher for a larger exposed surface area of the metal. After a subsequent calcination in an air flow at 800°C, the intensity of the TPR peak remained as small as that after the calcination at 950°C. This indicates that the metal sintering that occurred

over the SiO₂ supported Rh catalyst was irreversible. However, over the alumina supported Rh catalyst, the intensity of the TPR peak decreased to some extent (compared to that of the TPR peak of the catalyst calcined at 800°C for 4 h) after the catalyst was calcined in an air flow at 950°C, but it was almost restored to a level comparable to that observed in the first TPR run after a subsequent calcination in an air flow at 800°C. While no strong interactions could be identified on the alumina supported Rh catalyst, the latter catalyst exhibited resistance to metal sintering compared to the silica supported one, probably because of the comparable but opposite effects of the reductive and oxidative atmospheres (10). As already reported, alumina has a much higher stability than silica (1).

5. CONCLUSION

The interactions between Rh₂O₃ and various substrates were investigated by TPR and XRD. These investigations have shown that, for certain supports, compounds were generated between Rh₂O₃ and support at suitable calcination temperatures which were dependent upon the nature of the substrate. The paper demonstrates that the strong interactions resulting from the formation of compounds in-

crease the stability of the catalysts. Rh catalysts supported on Y₂O₃ and Ta₂O₅ exhibited higher rates of deactivation at a reaction temperature of 750°C than at 850 and 900°C, respectively. The TPR and XRD experiments indicated that compounds did form at 850 and 900°C, respectively, but not at 750°C.

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