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ScienceDirect

Catalysis Today 116 (2006) 341–347

CATALYSIS TODAY

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Spillover of labile OH, H, and O species in the H_2 production by steam reforming of phenol over supported-Rh catalysts

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Abstract

The aim of this work was to probe the back-spillover of labile O, OH and H species during steam reforming of phenol towards H_2 production in the 773–1028 K range over Rh supported on MgO and Mg-Ce-Zr-O mixed-metal oxides. This was made possible through steady state isotopic transient kinetic analysis (SSITKA) and other transient isotopic experiments (use of D_2O and $^{18}O_2$) combined with temperature-programmed desorption ones. The size of the active pool of H-containing intermediate species (H and/or OH) present in the H-path of reaction as a function of reaction T was measured over the 0.1 wt% Rh/50Mg-25Ce-25Zr-O catalyst by SSITKA experiments. It was found that the size of this pool decreases by 18% in the 773–928 K range ($\theta = 68.9–56.3$), whereas a significant decrease (by a factor of 10) was observed between 928 and 1028 K. These results demonstrate that most of the active H and OH species reside on the support and metal-support interface. Two kinds of H-containing intermediate species are likely to participate in the H-path of reaction. An inverse D kinetic isotopic effect was measured for the H_2 formation in the phenol steam reforming reaction in the 773–1028 K range.

Keywords: Oxygen spillover; OH spillover; Phenol steam reforming; Hydrogen production; SSITKA; Kinetic isotope effect

1. Introduction

Nowadays, there is an increasing interest in the use of renewable energy sources in order to gradually substitute in part fossil fuels. The production of a H_2-rich gas by biomass gasification processes is expected to play an important role towards future H_2 demands, including fuel cell applications. Pyrolysis of biomass has several environmental advantages over fossil fuels, namely low emissions of CO_2 and other greenhouse gases [1]. However, the formation of tar remains a severe problem in biomass gasification processes, where phenol is a major constituent of tar. Therefore, catalytic steam reforming of phenol towards further H_2 formation with the clean-up of gasification/reforming product gas at the same time are highly desirable. We have recently reported [2,3] on the development of novel supported-Rh catalysts of low metal loading (e.g., 0.1 wt%) for the selective steam reforming of phenol into H_2 gas. These catalysts were found to favourably compete with Ni-based industrial catalysts having nickel loadings larger than 30 wt%.

Labile O and OH species of support are usually speculated of being *true active reaction intermediates* in the steam reforming of hydrocarbons and oxygenates over metal oxide-supported metals. We have recently reported [4] *for the first time* that spillover of labile O and/or OH species from MgO and Mg-Ce-Zr-O mixed-metal oxides onto the Rh surface must be considered as a true mechanistic reaction path in the steam reforming of phenol towards H_2 formation. The use of steady state isotopic transient kinetic analysis (SSITKA) technique [5] allowed the measurement of the size (μmol/g) of the pool of true active H-containing intermediate species under reaction conditions (0.5%C_6H_5OH/40%H_2O/Ar, $T = 848–1028$ K). The size of this H-pool was found to be significantly larger than the equivalent amount of one surface Rh monolayer (μmol Rh_s/g). It becomes obvious that this large pool of H-containing intermediate species cannot reside on the Rh surface but almost all of it must reside on the support as hydroxyl species. In the case of 0.1 wt% Rh supported on the 50Mg-25Ce-25Zr-O mixed-metal oxide (MgO, $Mg_xZr_{1-x}O_2$, and $Ce_xZr_{1-x}O_2$ solid phases), it was estimated that 56.5 equivalent surface Rh monolayers of active H-containing species participate in the

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doi:10.1016/j.cattod.2006.05.079

H-reaction path for H_2 gas formation at $T = 923$ K [4]. It was also shown [4] that labile atomic oxygen species of Mg-Ce-Zr-O support which were first exchanged with ^{18}O from the gas phase participated in the formation of $C^{18}O$ and $C^{18}O_2$ when C_6H_5OH/H_2O gas mixture was passed over the Rh/Mg-Ce-Zr-O catalyst at 873 K. It was concluded that these labile atomic oxygen species spill over onto the Rh surface where they react with the deposited hydrocarbon-derived fragments ($–C_xH_y$), the latter formed after phenol adsorption and decomposition to form CO and CO_2.

The present work is a continuation of the work recently reported [4] major results of which were mentioned in the previous paragraph, aiming at providing further experimental evidence on the existence of a spillover mechanism of labile O and/or OH species from MgO and Mg-Ce-Zr-O mixed-metal oxide surfaces used as supports of Rh for the steam reforming of phenol in the 773–1028 K range. Furthermore, the dependence of the size of the active pool of H-containing intermediate species found in the hydrogen reaction path on reaction T is now established in the whole temperature range of 773–1028 K. In the present work, the number of different such active H-containing species was probed by temperature-programmed desorption (TPD) experiments after the catalyst surface was pretreated with D_2O(g) at 873 and 1003 K.

2. Experimental

2.1. Catalysts synthesis and characterization

50Mg-25Ce-25Zr-O mixed-metal oxide and pure MgO were prepared by sol–gel methods using $Ce(NO_3)_3 \cdot 6H_2O$, $Zr(OCl)_2 \cdot 8H_2O$ and $Mg(OEt)_2$ (Aldrich) as precursors of Ce, Zr and Mg, respectively [2,3]. For the 50Mg-25Ce-25Zr-O mixed-metal oxide, the metal atom% composition was 50, 25 and 25%, respectively, for Mg, Ce and Zr. After synthesis and drying (overnight at 393 K) the solids were calcined in air at 1023 K for 4 h, cooled to room temperature and stored for further use. Supported-Rh catalysts were prepared by the wet impregnation method [2,3]. Prior to any catalytic experiment the fresh catalyst sample was reduced in H_2 at 573 K for 2 h.

The BET areas of 50Mg-25Ce-25Zr-O and MgO supports were found to be 30.5 and 27.7 m^2/g, respectively. The Rh dispersions of fresh and used (after about 10 h of reaction in the 773–1028 K range) 0.5 wt% Rh/MgO catalysts were found to be 60 and 35%, respectively. In the case of 0.1 wt% Rh/50Mg-25Ce-25Zr-O catalyst, 90 and 50% Rh dispersions, respectively, were measured. The crystal structure of the 50Mg-25Ce-25Zr-O solid support consisted of MgO, $Ce_xZr_{1-x}O_2$ and $Mg_xZr_{1-x}O_2$ phases, according to XRD studies [3].

2.2. Mechanistic and temperature-programmed desorption studies

The transient flow-system, micro-reactor and analysis system used for conducting mechanistic and temperature-programmed desorption studies were described in detail elsewhere [2]. SSITKA experiments were performed using two HPLC pumps (GILSON pump 307) for the addition of water or D_2O (e.g., phenol/H_2O or phenol/D_2O mixture) to the reactor feed stream. The dry gas stream from the exit of a condenser placed downstream the reactor was directed to a mass spectrometer (Baltzers-Omnistar^{TM}) for *on line* measurements of H_2, CO and CO_2 normal and isotopic (D and ^{18}O) species [4].

3. Results and discussion

The main objective of the present work was to provide fundamental information in terms of elementary steps, kinds and surface coverage of active H-containing intermediate species as a function of reaction temperature for the steam reforming of phenol based on the following reaction network [6,7]:

$$C_6H_5OH + 5H_2O \rightarrow 6CO + 8H_2 \quad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (2)$$

The SSITKA technique [5] was used to follow the reaction H-path according to the gas switch 0.5%C_6H_5OH/40%D_2O/Ar/Kr (T, 30 min) → 0.5%C_6H_5OH/40%H_2O/Kr (T, t) (coded as $F_A \rightarrow F_B$). Fig. 1 presents dimensionless transient response curves of gas phase H_2, HD and D_2 obtained on the 0.1 wt% Rh/50Mg-25Ce-25Zr-O catalyst during SSITKA experiments at

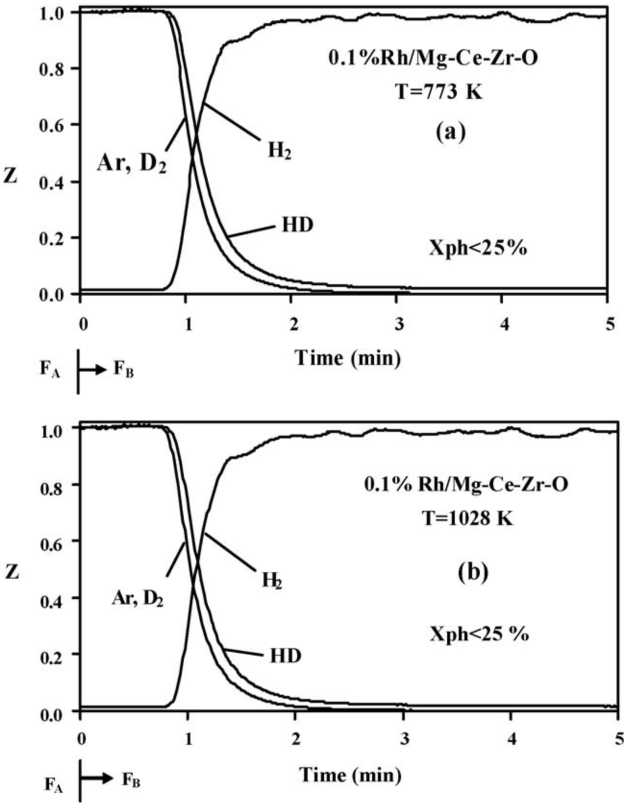

Fig. 1. Dimensionless transient response curves of H_2, HD and D_2 obtained during SSITKA experiments at 773 K (a) and 1028 K (b) over the 0.1 wt% Rh/50Mg-25Ce-25Zr-O catalyst. $F_A = 0.5\%$ C_6H_5OH/40% D_2O/Ar/Kr, $F_B = 0.5\%$ C_6H_5OH/40% H_2O/Kr. The dimensionless transient response curve of Ar diluent gas is also shown. The conversion of phenol (X_{ph}) was kept less than 25%.

773 K (Fig. 1a) and 1028 K (Fig. 1b), where phenol conversion was kept below 25%. The Z parameter shown in y-axis is a dimensionless concentration defined by the following relationship:

$$Z = \frac{y(t) - y_\infty}{y_0 - y_\infty} \tag{3}$$

where $y(t)$ is the mole fraction of a given gaseous species after the switch $F_A \rightarrow F_B$ was made, whereas y_0 and y_∞ are the mole fractions of the given species before the switch and long after the switch (a new steady state is achieved under the non-isotopic feed gas mixture, F_B), respectively. Thus, the Z parameter takes values between 1 and 0. The Ar transient response curve describes the hydrodynamic behaviour of the flow-system from the chromatographic switching valve to the mass spectrometer (through the reactor with the catalyst in place), and accounts for the gas hold-up in the gas lines and the reactor volume. As clearly seen in Fig. 1 (Ar curve), the down-step isotopic switch is not a perfect step function due to various mixing effects in the gas lines and the reactor [5]. Integration of the HD and D_2 response curves relative to the Ar curve should provide the size of the active pool of D-containing intermediate species (D and/or OD) after using the following material balance equation:

$$N_D\,(\mu\text{mol}) = F_A(y_0^{HD} - y_\infty^{HD}) \int_0^{t_{ss}} (Z_{HD} - Z_{Ar})\,\mathrm{d}t \tag{4}$$

where y_0^{HD} is the steady state mole fraction (in units of ppm) of HD gas produced under the isotopic feed gas composition F_A (mol/min) used, whereas t_{ss} is the time required for the new steady state to be achieved under the non-isotopic feed gas composition F_B (mol/min). It is noted that in Eq. (4) the corresponding term based on the D_2 transient response curve is not given since the Z_{D_2} and Z_{Ar} response curves were found to be identical (Fig. 1). The amount of N_D was found to be 603.1 μmol/g ($\theta_D = 68.9$) and 48.9 μmol/g ($\theta_D = 5.6$) at 773 and 1028 K, respectively. Here, the equivalent number of surface Rh monolayers (θ) is estimated based on the amount of surface Rh atoms per gram of catalyst measured by H_2 chemisorption (8.74 μmol Rh_s/g) [2–4] and corresponds to the fresh catalyst state. The latter is appropriate since for every reaction T a fresh catalyst sample was used for each SSITKA experiment performed.

It is pointed out that the $D_2(g)$ response curve is identical to the Ar curve meaning that chemisorption and dissociation of H_2O must be very fast steps, thus providing enough H-containing intermediate species that make their recombination with a D-containing intermediate species much more probable than the recombination of two adjacent D-containing intermediate species. The evolution of H_2 gas response curves according to Fig. 1a and b are similar, suggesting that in the temperature range 773–1028 K the product of kinetic rate constant (k) of the rate-limiting step and of the size (N_H, μmol/g) of the active H-containing intermediate species pool stays practically constant. This is true assuming that the rate of reaction can be described adequately by the relationship: rate = kN_H, where k is an effective kinetic rate constant.

Similar SSITKA experiments to those of Fig. 1 performed over the 0.5 wt% Rh/MgO catalyst at 923 and 1028 K [4] revealed a time delay in the appearance of the transient production of HD and H_2 gases compared to the present 0.1 wt% Rh/Mg-Ce-Zr-O catalyst (Fig. 1); for the latter no time delay is seen, where hydrogen production starts at exactly the same time the Ar response starts to fall off. These results illustrate mainly the influence of support in determining the rate of hydrogen production through the spillover of OH/H active intermediate species.

Fig. 2 reports the effect of reaction T on the size (in terms of equivalent number of surface Rh monolayers, θ) of the active pool of H-containing intermediate species in the 773–1028 K range. It is clearly observed that the size of D-pool decreases significantly with reaction T. In particular, there is a decrease by a factor of 12.3 by increasing the reaction T from 773 to 1028 K. This is suggested to be due to the lower degree of surface hydroxylation with increasing T under steady state reforming reaction conditions. Sintering of Rh small crystallites at 1028 K during the 30 min reaction time could partly explain the significant decrease of the size of the D-pool, where an increase of Rh particle size beyond a critical value may exclude an amount of OH and/or H species to diffuse from the support surface onto the surface of Rh metal crystallites to form H_2 gas. This possibility was checked experimentally as follows. After the SSITKA experiment at 1028 K was performed, a similar experiment was subsequently performed at 773 K. It was found that the D-pool size was within 10% of that measured on the fresh solid sample. Therefore, the results of Fig. 2 are practically free of small variations of Rh particle size with reaction temperature that could influence the size of the D-pool.

Based on the results of Fig. 2, it is demonstrated that the major part of OH and/or H-pool must reside on the support and the metal-support interface; one surface Rh monolayer of OH and/or H species ($\theta = 1$) corresponds to 15 and 2%, respectively, of the total number of surface Rh monolayers measured at 1028 and 773 K. A back-spillover process of H and/or OH species

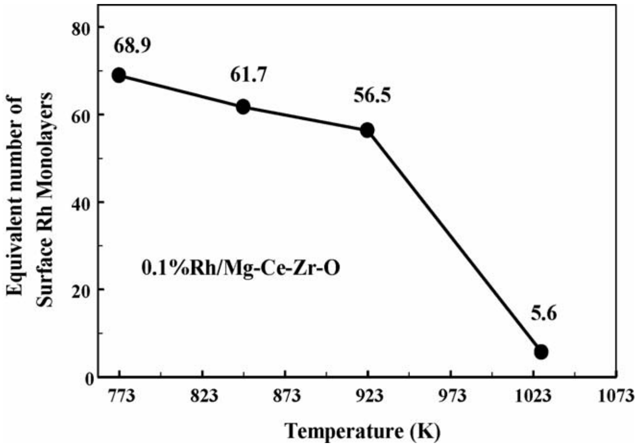

Fig. 2. Effect of reaction temperature on the size of D-pool (expressed in equivalent number of surface Rh monolayers) determined by SSITKA experiments in the 773–1028 K range over the 0.1 wt% Rh/50Mg-25Ce-25Zr-O catalyst.

from the support to the Rh metal comes therefore as a logical explanation of the large quantity of the H-pool measured.

It is important to mention here that at 923 K the specific integral hydrogen production rate (mmol H_2/m^2 min) obtained with the 0.1 wt% Rh/50Mg-25Ce-25Zr-O catalyst is more than 10 times larger than that obtained with the 50Mg-25Ce-25Zr-O support alone. Similar results were obtained for the other temperatures shown in Fig. 2 and for the MgO support as well. Therefore, these results illustrate that the support alone acts as the main source of active H-containing intermediate species for the steam reforming of phenol activity over Mg-Ce-Zr-O and MgO-supported Rh catalysts, with a minor only contribution in promoting the rate of reaction on its surface alone.

It is well known that water adsorbs dissociatively on metal oxide surfaces according to the following elementary reaction step [8–10]:

$$H_2O(g) + S_2 + O_L \rightarrow HO_{-S_2} + H - O_L \tag{5}$$

where S_2 is a metal cation and O_L is a surface lattice oxygen of support. The OH and H back-spillover processes are described by Eqs. (6) and (7), where S_1 is a Rh atom. It is important to note here that both OH and H species must spill over the Rh surface in order that a mass balance among Eqs. (5)–(7) at steady state reaction conditions is to be retained. Otherwise, back-spillover of only the OH or H species would eventually lead to the saturation of support surface via protonation or hydroxylation, respectively, thus terminating reaction step (5).

$$HO_{-s_2} + S_1 \rightarrow HO_{-s_1} + S_2 \quad \text{(OH back-spillover)} \tag{6}$$

$$H - O_L + S_1 \rightarrow H_{-s_1} + O_L \quad \text{(H back-spillover)} \tag{7}$$

Reference to the above-described elementary reaction steps of water dissociation on the metal-oxide support surface does not imply that in the present catalytic system water dissociation on the Rh surface alone cannot take place. Here it is pointed out that the specific role of water in the overall reaction network is rather associated with the support than the Rh metal surface. The latter is mainly covered by adsorbed hydrocarbon fragments derived from the decomposition of adsorbed phenol molecules [11].

An inverse kinetic isotopic effect (KIE) for the production of hydrogen, $R_{H_2}/R_{D_2} = 0.65$ and 0.75 at 773 and 1028 K, respectively, was obtained over the Rh/Mg-Ce-Zr-O catalyst (based on SSITKA measurements, Fig. 1). This result has been discussed and explained in detail in our previous publication [4].

Fig. 3 presents temperature-programmed desorption curves of H_2, HD and D_2 for the 0.5 wt% Rh/MgO catalyst. After catalyst exposure to 40%D_2O/Ar mixture at 873 K (Fig. 3a) or 1003 K (Fig. 3b) for 20 min, purge in Ar for 10 min followed by cooling to 473 K in Ar flow, the temperature of the catalyst was then increased to 1023 K (β = 20 K/min). The shape of the TPD curves obtained over the Rh/MgO catalyst was found to strongly depend on the temperature the catalyst was treated with D_2O. In the case of 873 K (Fig. 3a), one symmetrical desorption peak (T_M = 1023 K) for each isotopic di-hydrogen species was obtained. The amount of D-containing species (estimated from the HD and D_2 response curves) was found to be 1202 μmol D/g (θ_D = 70.6, based on Rh dispersion of used catalyst). On the other hand, the TPD curves obtained after catalyst treatment with D_2O at 1003 K (Fig. 3b) appears to be completely different compared with those obtained after catalyst treatment at 873 K (Fig. 3a). The TPD curves now consists of two peaks (not well resolved) in all HD, D_2 and H_2 response curves, as opposed to one distinct peak in the case of catalyst treatment with D_2O at 873 K. In the case of D_2 response curve, the first peak is centered at 943 K and the second peak at 1023 K. In the case of HD response curve, the first peak is centered at 1003 K and the second one at 1023 K. The amount of D-containing active species was found to be 1606 μmol D/g (θ_D = 94.4).

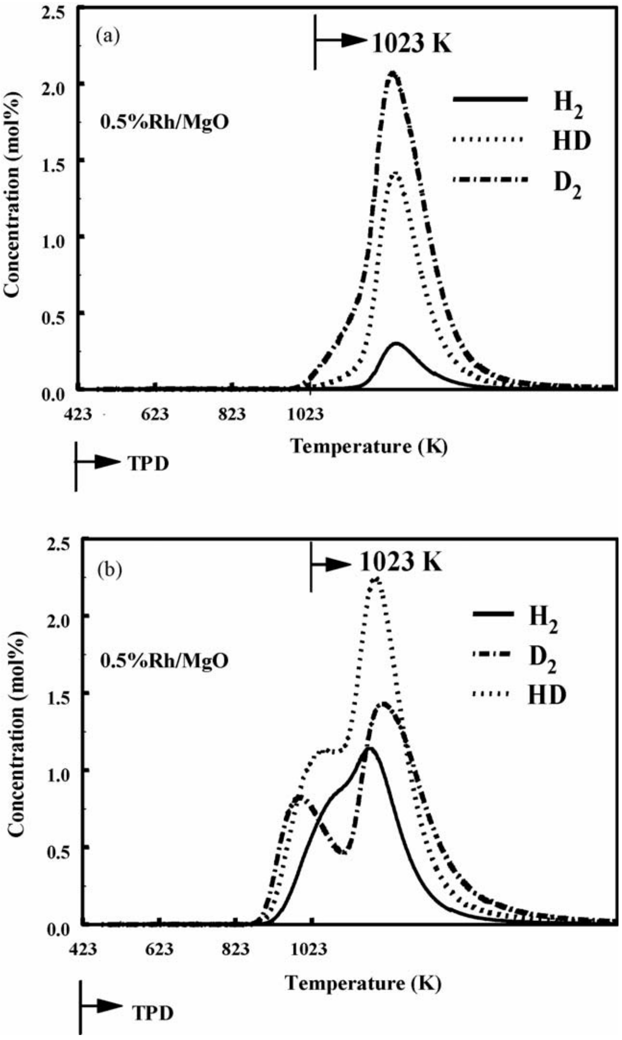

Fig. 3. Temperature-programmed desorption response curves of H_2, HD and D_2 gaseous species obtained on the 0.5 wt% Rh/MgO catalyst according to the gas delivery sequence: 40% D_2O/Ar (T, 20 min) → cool down quickly in Ar flow to 423 K → TPD in Ar (β = 2 K/min). (a) T = 873 K; (b) T = 1003 K.

The results of Fig. 3a and b suggest that new active sites for D_2O adsorption and dissociation are populated with increasing adsorption temperature. According to the model proposed by Coluccia and Tench for the MgO surface [12], there are several ionic pairs of Mg-O with different coordination numbers. Ionic pairs with low coordination appear at corners, edges and in crystal faces of high Miller indices. This inherent surface heterogeneity is directly correlated with the different TPD profiles shown in Fig. 3, the latter associated with the different bond strengths of surface –O and –OH species. It could be proposed that reaction temperature of the phenol steam reforming reaction plays a role in determining the kinds and concentration of –O and/or –OH species that spill over from the MgO support onto the Rh surface.

Fig. 4 presents TPD curves of H_2, HD and D_2 obtained over the 0.1 wt% Rh/Mg-Ce-Zr-O catalyst after conducting exactly the same experiment as in the case of 0.5 wt% Rh/MgO (Fig. 3b). The TPD profiles obtained are characterized by a small HD desorption peak centered at 1023 K, whereas the D_2 and H_2 response curves exhibit two peaks with maxima at 548 and 1023 K. The amount of D-containing species was found to be 137.7 μmol/g ($\theta_D = 28.3$).

The main differences between the 0.5 wt% Rh/MgO and 0.1 wt% Rh/Mg-Ce-Zr-O catalysts is the appearance of the first H_2 and D_2 desorption peaks at significantly different T_M values (548 K versus 943 K), and the amount of D species that participate in the formation of isotopic di-hydrogen molecular species. These differences could be mainly attributed to the different support surface physicochemical properties and to a lesser extent to the Rh metal particle size. According to XRD studies [3], the main crystal phases of 50Mg-25Ce-25Zr-O support were found to be MgO, $Ce_xZr_{1-x}O_2$ and $Mg_xZr_{1-x}O_2$. The presence of these phases increase the surface heterogeneity of the solid with respect to the kinds of labile –O and –OH species, and it is suggested to be the main reason for the appearance of the H_2 and D_2 desorption peaks at the low peak maximum temperature of 623 K. For the phenol steam reforming reaction, the back-spillover of –O and/or –OH species has a key role to play as discussed previously and in our recent publication [4], subject that will also be presented and discussed next. It should also be pointed out that back-spillover of a given species is greatly facilitated by the contact area of metal-support phases, the latter being affected by the metal particle size and morphology. It is pointed out here that the D-pool that forms di-hydrogen isotopic species (D_2 and HD) in the experiments reported in Figs. 3 and 4 is larger in the case of Rh/MgO (Fig. 3) compared to Rh/Mg-Ce-Zr-O (Fig. 4) solid. This result is just the opposite in the case of the active D-pool participating in the steam reforming of phenol as revealed by the SSITKA experiments (Fig. 1). Therefore, it could be stated that in the case of MgO support not all the D-pool participates in the steam reforming of phenol reaction. In the case of Mg-Ce-Zr-O support, the size of the D-pool is enhanced under steam reforming of phenol reaction conditions.

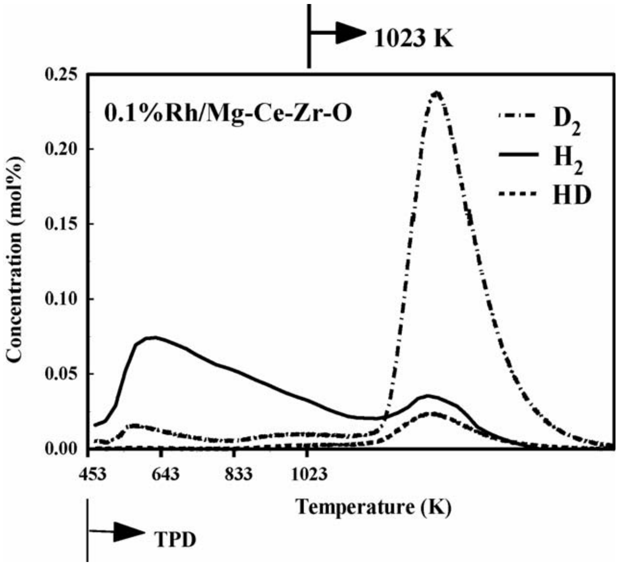

Fig. 4. Temperature-programmed desorption response curves of H_2, HD and D_2 gaseous species obtained on the 0.1 wt% Rh/50Mg-25Ce-25Zr-O catalyst according to the gas delivery sequence: 40% D_2O/Ar (1003 K, 20 min) → cool cool down quickly in Ar flow to 453 K → TPD in Ar ($\beta = 20$ K/min).

The possible contribution of oxygen vacancies and/or labile oxygen species of MgO support during phenol steam reforming reaction over the Rh/MgO catalyst was probed by the following isotopic experiment: 3%$^{18}O_2$/Ar (T, 20 min) → He (T, 15 min) → 0.5%C_6H_5OH/40%H_2O/Ar (T, t). The amount of isotopic $C^{18}O$, $C^{18}O^{16}O$ and $C^{18}O_2$ species produced during the latter switch corresponds to the amount of ^{18}O spilt from the support over to the Rh metal surface during steam reforming. However, part of the amount of isotopic $C^{18}O_2$ and $C^{18}O^{16}O$ species produced after the switch to the phenol/water mixture might be the result of the direct exchange of ^{16}O of the $C^{16}O_2$ molecule with adsorbed ^{18}O species (e.g., $C^{16}O_2(g) + {}^{18}O\text{-s} \rightarrow C^{16}O^{18}O(g) + {}^{16}O\text{-s}$). In order to account for this effect, the following experiment had been conducted. After treatment of the catalyst surface with 3%$^{18}O_2$/Ar at a given T for 20 min, the feed was changed to pure He for 15 min. The feed was then switched to a y%CO_2/40%H_2O/Ar gas mixture and at the same time all the oxygen isotopic CO_2 species were followed by on line mass spectrometry. The y mol% CO_2 used in the latter feed gas composition was that measured during steady state 0.5%C_6H_5OH/40%H_2O/Ar reaction at the same reaction temperature. The amount of ^{18}O estimated from this experiment was subtracted from the amount estimated in the previously described transient isotopic experiment, and this is referred to the net amount of ^{18}O species.

Fig. 5 presents transient response curves of $C^{18}O$, $C^{16}O^{18}O$, $C^{18}O_2$ and $C^{16}O$ obtained on the 0.5 wt% Rh/MgO at 873 K after the 3%$^{18}O_2$/Ar → He → C_6H_5OH/H_2O/Ar (t) sequence of gas switches was applied. These response curves correspond to the last gas switch as indicated in the bottom of Fig. 5. The net amount of ^{18}O was found to be 64.4 μmol/g, $\theta = 2.2$ (based on the Rh dispersion of fresh catalyst). We have already reported [4] that the corresponding amount in the case of 0.1 wt% Rh/Mg-Ce-Zr-O was 159.5 μmol/g, $\theta = 18.2$ (based on the Rh dispersion of fresh catalyst). It is important to point out that the concentration of CO_2 used in the y%CO_2/40%H_2O/Ar switch is the maximum expected to be formed under the 0.5%C_6H_5OH/40%H_2O/Ar treatment. Therefore, the ^{18}O-pool expressed in terms of θ is a lower and not an upper limit. The fact that the Rh/Mg-Ce-Zr-O solid presents a larger amount of labile/exchangeable oxygen species compared to Rh/MgO agrees very well with the H_2 TPR results reported elsewhere [13], where an

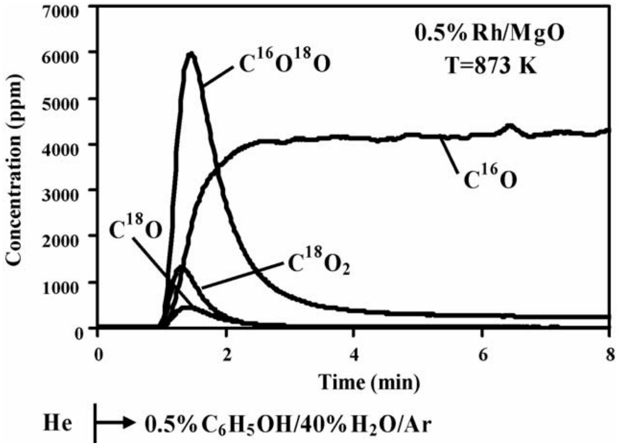

Fig. 5. Transient response curves of $C^{18}O$, $C^{16}O^{18}O$, $C^{18}O_2$ and $C^{16}O$ obtained over the 0.5 wt% Rh/MgO catalyst according to the gas delivery sequence: 3% $^{18}O_2$/Ar (873 K, 20 min) → Ar (873 K, 15 min) → 0.5% C_6H_5OH/40% H_2O/Ar (873 K, *t*).

amount of 3.8 and 0.02 mmol O/g of reducible oxygen species in the 373–1073 K range was measured in the case of Rh/Mg-Ce-Zr-O and Rh/MgO solids, respectively.

As discussed previously for the differences in the characteristics of the transient response curves of HD and H_2 obtained during SSITKA experiments (Fig. 1) for the Rh/MgO and Rh/Mg-Ce-Zr-O catalysts, large differences in the rate of $C^{16}O$ formation are observed (compare Fig. 5 and Fig. 2 (Ref. [4]). In the case of Rh/Mg-Ce-Zr-O catalyst, a very sharp increase in the concentration of $C^{16}O$ formed was observed with the appearance of a maximum in the rate of $C^{16}O$ formation after about 2 min from the switch He → C_6H_5OH/H_2O/He (*t*). On the other hand, in the present case of Rh/MgO (Fig. 5), the rate of $C^{16}O$ starts from a very low value and increases with an exponentially-like manner. It is suggested that the different labile oxygen species present in MgO, $Mg_xZr_{1-x}O_2$ and $Ce_xZr_{1-x}O_2$ solid phases determine the transient rate of back-spillover of oxygen from these support phases onto the Rh metal that react with hydrocarbon-derived fragments from phenol decomposition [11] to form CO and CO_2. It is suggested that the rate of back-spillover of labile oxygen species largely determines the overall rate of CO and CO_2 formation.

It is therefore clear that the major part of ^{18}O-pool appeared during the 0.5%C_6H_5OH/40%H_2O/Ar switch had been adsorbed on oxygen vacant sites and/or exchanged with labile oxygen of MgO support during the 3%$^{18}O_2$/Ar treatment. Based on the previous discussion, it is logical to suggest that these oxygen vacancies and labile oxygen species are expected to play a significant role in the decomposition of water and in turn in the steam reforming of phenol reaction. Water can adsorb onto oxygen vacancies to form labile –OH species according to the following Eq. (8) [14]:

$$H_2O(g) + O_L + \Box_s \rightarrow HO/\Box_s + HO_L \qquad (8)$$

where, $\Box_s$ is an oxygen vacant site on the support. The latter labile $HO/\Box_s$ species are expected to diffuse more easily onto the Rh surface compared with HO_L associated with surface lattice oxygen. It is suggested that supported-metal catalysts with supports that possess a large concentration of oxygen vacancies and/or labile oxygen are expected to favour phenol steam reforming reaction in the 773–1023 K range. The latter was confirmed in our recent studies over supported-Rh catalysts [2,3]. It should be mentioned that dissociation of water via Eq. (8) is expected to occur to a larger extent on the Mg-Ce-Zr-O support that possesses an increased concentration of oxygen vacant sites (e.g., through mainly the $Ce_xZr_{1-x}O_2$ phase) as compared to MgO solid for which dissociation of water is expected to proceed mainly via Eq. (5). The large differences in the desorption curves of di-hydrogen isotopic species presented in Figs. 3b and 4 for the two solids is related to the dissociation steps (5) and (8) mentioned above.

An interesting mechanistic point that could be considered is that of the spillover of hydrocarbon-derived fragments from phenol decomposition onto the Rh surface to the metal oxide support surface/interface to get oxidized by labile O and OH species to form CO, CO_2 and H_2. This consideration is not in contradiction with the large H-pool of active species measured by SSITKA experiments (Fig. 1). However, such a consideration requires that the bond strength of –C_xH_y species with the Rh surface is lower than that of –OH with the metal oxide surface, and also that of H with the O atom in the –OH adsorbed species. Furthermore, diffusion of –C_xH_y species from the Rh metal to the support surface must be considered of lower energy barrier requirements than those of –OH and/or H species. These ideas need to be elaborated by quantum chemical calculations, since SSITKA experiments by labelling the carbon atoms of phenol (^{13}C) would not be decisive as to the occurrence of a spillover of –C_xH_y active intermediate species from the metal to the support metal oxide surface. On the other hand, the water–gas shift (WGS) reaction (2) present in the reaction network could proceed via a formyl and/or formate intermediate species on the support alone and on the supported-Rh catalyst as well for H_2 and CO_2 formation [15,16]. The latter brings about the important question about the exact OH/H pool size of intermediate species that participate via a spillover mechanism in the H-path of reaction as compared with that of other H-containing intermediate species (e.g., formates). The answer to this cannot be provided from the SSITKA results of the present work (Fig. 1).

4. Conclusions

The following conclusions can be derived from the results of the present work:

(a) A large pool (exceeding several monolayers of surface Rh) of active H-containing (H and/or –OH) intermediate species mainly residing on the 50Mg-25Ce-25Zr-O and MgO supports participate in the H-path of phenol steam reforming reaction towards H_2 gas formation over Rh/MgO and Rh/Mg-Ce-Zr-O catalysts.

(b) An inverse deuterium Kinetic Isotopic Effect for the production of H_2 gas was measured during steam reforming of phenol in the 773–1028 K range over 0.5 wt% Rh/MgO and 0.1 wt% Rh/Mg-Ce-Zr-O catalysts.

(c) The back-spillover process of labile –OH, H and –O species from MgO and 50Mg-25Ce-25Zr-O supports onto the Rh metal surface was proven by various transient isotopic and temperature-programmed desorption experiments. The kinds of –OH and/or –O species and their amounts are largely affected by the reaction temperature and support chemical composition.

Acknowledgments

We acknowledge the financial support by the European Union (5th FP) through the ENK-5-CT-2001-00545 research project, and by the Research Committee of the University of Cyprus.

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