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Catalysis Today 112 (2006) 89–93

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# The role of oxygen and hydroxyl support species on the mechanism of $H_2$ production in the steam reforming of phenol over metal oxide-supported-Rh and -Fe catalysts

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## Abstract

The aim of this work was to probe *for the first time* the back-spillover of labile O and OH species during steam reforming of phenol towards $H_2$ production over Rh and Fe supported on MgO, Mg-Ce-O and Mg-Ce-Zr-O metal oxides. This was made possible through SSITKA and other transient isotopic experiments (use of $D_2O$ and $^{18}O_2$). The size of the active pool of H-containing species (H and/or OH) present under reaction conditions as a function of reaction $T$ and catalyst composition, and deuterium kinetic isotope effects were measured.

*Keywords:* Oxygen spillover; OH spillover; Steam reforming; Phenol; 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 in biomass gasification processes is expected to play an important role towards future $H_2$ demands, including fuel cell applications. The formation of tar remains a severe problem in biomass gasification processes. In many cases, phenol is the major constituent of tar. It appears, therefore, that steam reforming of phenol towards further $H_2$ formation and its elimination from the gasification/reforming product gas are highly desirable. We have recently reported [1,2] on the development of supported-Rh catalysts of low metal loading for the selective steam reforming of phenol into $H_2$ gas. These catalysts were found to favorably compete with Ni-based industrial catalysts (>40 wt% Ni).

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. It has been reported [3,4] that the reverse spillover of OH species in the $H_2O$ and $CO_2$ reforming of $CH_4$ reactions over supported-Ni catalysts is an important mechanistic step. This spillover step during steam reforming of phenol has not yet been investigated, especially with the use of SSITKA techniques.

The aim of this work was to probe *for the first time* the back-spillover of labile O and OH species during steam reforming of phenol over active Rh and Fe supported on MgO, Mg-Ce-O and Mg-Ce-Zr-O metal oxides [1,2,5]. This was made possible through SSITKA and other transient isotopic experiments (use of $D_2O$ and $^{18}O_2$). The size of the active pool of H-containing species (H and/or OH) present under reaction conditions as a function of reaction $T$ and catalyst composition, and deuterium kinetic isotope effects were measured.

## 2. Experimental

### 2.1. Catalysts synthesis and characterization

#### 2.1.1. Catalysts synthesis

Mg-Ce-Zr-O, Mg-Ce-O and pure MgO supports 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 [1,2]. The metal atom% composition was 50Mg-25Ce-25Zr-O and 50Mg-50Ce-O. After synthesis and drying (overnight at 120 °C), the solids were calcined in air at 750 °C for 4 h, slowly cooled to room temperature and stored

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doi:10.1016/j.cattod.2005.11.037

for further use. The supported-Rh and -Fe catalysts where prepared by the wet impregnation method using $Rh(NO_3)_3$ and $Fe(NO_3)_3\cdot H_2O$ (Aldrich) metal precursors, respectively. After impregnation and drying overnight at 120 °C, the obtained solid was calcined in air (600 °C, 2 h) and stored for further use. Prior to any catalytic tests, the fresh sample was reduced in $H_2$ (300 °C, 2 h).

### 2.1.2. Catalysts characterization

The BET area ($m^2\ g^{-1}$) of Mg-Ce-Zr-O, Mg-Ce-O and MgO supports was checked by $N_2$ adsorption at 77 K using a multipoint Fisons Sorpty 1900 System. Metal dispersions of fresh and used catalysts were determined by $H_2$ chemisorption followed by TPD in He flow [1,2]. Results on X-ray diffraction, SEM and HRTEM studies performed have been described elsewhere [1,2].

### 2.2. Mechanistic reaction studies

The Microreactivity Pro apparatus (CSIC-Spain), transient flow-system, microreactor and analysis system used for conducting mechanistic catalytic studies were described in detail elsewhere [1]. SSITKA experiments were performed using two HPLC pumps (GILSON pump 307) for the addition of water and $D_2O$ (Aldrich, 99.96% D) to the reactor feed stream. An appropriate amount of phenol (BDH, 99%) was dissolved in water or $D_2O$ to form a 5.9 wt% solution. 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 isotope-containing (D, $^{13}C$, $^{18}O$) species. Calibration of $D_2$ response was made using a 5% $D_2$/Ar (Spectra Gases) calibration gas mixture.

## 3. Results and discussion

### 3.1. Catalysts characterization

The BET areas ($m^2$/g) of 50Mg-25Ce-25Zr-O, 50Mg-50Ce-O and MgO supports were found to be 30.5, 79.8 and 27.7 $m^2$/g, respectively [1,2]. The Rh dispersion of 0.1 wt% Rh/Mg-Ce-Zr-O and 0.5 wt% Rh/MgO catalysts determined by $H_2$ chemisorption was found to be 90 and 60%, respectively, while that of Fe on the 5 wt% Fe/Mg-Ce-O catalyst was found to be 26%. HRTEM studies conducted over several supported-Rh catalysts confirmed the correctness of the $H_2$ chemisorption measurements [1,2].

### 3.2. Mechanistic studies

The main objective of the present work was to provide fundamental mechanistic information in terms of elementary reaction steps for the reaction network [6,7]:

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

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

SSITKA experiments [8] performed in order to follow the H-path involved the switch 0.5% $C_6H_5OH$/40% $D_2O$/Ar ($T$, $\Delta t$) → 0.5% $C_6H_5OH$/40% $H_2O$/Ar ($T$, $t$) (coded as $F_A \rightarrow F_B$, Expt A). Fig. 1 presents the transient response curves of $H_2$, HD and $D_2$ obtained on the 0.5 wt% Rh/MgO during SSITKA of phenol steam reforming at 650 °C (Expt A) at phenol conversion less than 25%. By integrating the HD and $D_2$ response curves relative to the response curve of a non-adsorbing/reacting gas [8], the *active pool* of H-containing intermediate species (H or/and OH) can be calculated. This was found to be 83.3 μmol/g ($\theta = 2.8$), where $\theta = 1.0$ refers to a monolayer of surface metal (Rh or Fe) determined by $H_2$ chemisorption (see Section 3.1). It is clear that the major part of H or/and OH pool must reside on the support and/or the metal–support interface. Thus, a back-spillover of H and/or OH species from the support to the Rh metal must at first be incorporated. Table 1 provides the size of the pool of active H-containing intermediate species (D-pool) determined for the present catalysts and for various reaction temperatures. In the case of supported-Fe catalyst, the size of this pool is significantly smaller compared to supported-Rh catalysts. It is speculated that the larger particle size of Fe (4.2 nm) compared to Rh (1.2 nm, 0.1 wt% Rh) is one of the factors that control the back-spillover rate of H-containing intermediate species.

It is well known [4,9,10] that water adsorbs dissociatively on metal oxide surfaces, according to the following elementary reaction step:

$$H_2O(g) + S_2 + O_L \rightarrow HO_{-S_2} + H{-}O_L \qquad (3)$$

where $S_2$ is a metal cation and $O_L$ is a surface lattice oxygen of support. The OH and H back-spillover reaction steps are described by Eqs. (4) and (5), where, $S_1$ is a Rh atom. It is important to note here that both OH and H species must spill over to the Rh surface in order to retain a mass balance between Eqs. (3)–(5) at steady-state reaction conditions. Otherwise, the 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 (3).

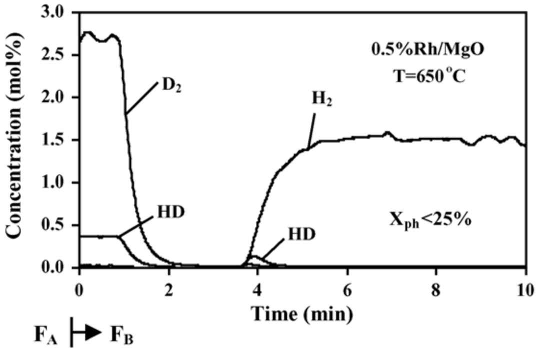

Fig. 1. Transient response curves of $H_2$, HD and $D_2$ obtained during SSITKA at 650 °C over 0.5 wt% Rh/MgO catalyst. $F_A$ = 0.5% $C_6H_5OH$/40% $D_2O$/Ar and $F_B$ = 0.5% $C_6H_5OH$/40% $H_2O$/Ar. The conversion of phenol ($X_{ph}$) was less than 25% in all SSITKA experiments.

Table 1
Amount (μmol/g) of isotopic labelled species formed during transient isotopic experiments

| Catalyst | $T$ (°C) | $^{18}O$ pool (μmol/g) (Expt C/Expt D) | Expt C − Expt D (μmol/g) | D pool (μmol/g) (Expt A) |
|---|---|---|---|---|
| 5% Fe/50Mg-50Ce-O | 550 | 13.2/12.5 | 0.7 ($\theta = 0.005$) | – |
| | 650 | 58.4/44.3 | 14.1 ($\theta = 0.06$) | 37.5 ($\theta = 0.17$) |
| | 700 | – | – | 22.5 ($\theta = 0.1$) |
| | 750 | – | – | 32.2 ($\theta = 0.14$) |
| 0.5% Rh/MgO | 450 | 44.8/23.2 | 21.6 ($\theta = 0.74$) | – |
| | 575 | – | – | 131.4 ($\theta = 4.5$) |
| | 600 | 166.8/102.4 | 64.4 ($\theta = 2.2$) | – |
| | 650 | – | – | 83.3 ($\theta = 2.8$) |
| | 755 | – | – | 85.3 ($\theta = 2.9$) |
| 0.1% Rh/50Mg-25Ce-25Zr-O | 450 | 61.6/39.0 | 22.6 ($\theta = 2.6$) | – |
| | 600 | 292.4/132.9 | 159.5 ($\theta = 18.2$) | – |
| | 650 | – | – | 493.9 ($\theta = 56.5$) |
| | 755 | – | – | 48.9 ($\theta = 5.6$) |

$$HO_{-S_2} + S_1 \rightarrow HO_{-S_1} + S_2 \quad \text{(OH back-spillover)} \tag{4}$$

$$H{-}O_L + S_1 \rightarrow H_{-S_1} + O_L \quad \text{(H back-spillover)} \tag{5}$$

According to Fig. 1, an inverse kinetic isotope effect (KIE) for the production of hydrogen ($R_{H_2}/R_{D_2} = 0.59$) is obtained over the Rh/MgO catalyst. This result can be explained as follows. The spillover of H is a well-known phenomenon on supported-metal catalysts, where high spillover rates can be obtained at high reaction temperatures [11,12]. On the other hand, the spillover of OH species is expected to be a more activated process. Therefore, the contribution of the latter process to the overall rate of phenol reforming towards $H_2$ production is expected to be more significant. The vibrational frequencies of bonded D and H on either Rh or surface lattice O species of support indicate that the Rh–D and O–D bond strengths are larger compared to the Rh–H and O–H ones [7,13]. Therefore, after dissociation of $D_2O$ (Eq. (3)) the D–O bond is expected to become stronger and at the same time the DO–$M^{n+}$ ($M^{n+}$ = metal cation of support) bond weaker. This in turn is expected to lead to a higher back-spillover rate of OD species to the Rh metal and likely to a higher OD coverage ($\theta_{OD}$). The higher $\theta_{OD}$ and the weaker Rh–OD bond will lead to higher reaction rates between the adsorbed intermediate OD and $CH_x$ species, the latter derived after phenol decomposition on the Rh metal (Eqs. (6)–(8)) [14]. This in turn will imply higher $H_2$ production rates, if the rate-determining step (RDS) of the overall reaction is one of the steps (6)–(8) and not the recombination of two adsorbed H species to form $H_2$ gas (step (9)). It is noted that an inverse KIE was also observed for the $CO_2$ product and similarly in all other catalysts examined (see Table 2).

$${}_{x}HC_{-S_1} + DO_{-S_1} \rightarrow {}_{x-1}HC_{-S_1} + HDO(g) + S_1 \tag{6}$$

$${}_{x-1}HC_{-S_1} + DO_{-S_1} \rightarrow \ldots\ldots\ldots \xrightarrow{DO_{-S_1}} CO_{-S_1} + HD(g) \tag{7}$$

$$CO_{-S_1} + DO_{-S_1} \rightarrow CO_2(g) + D_{-S_1} + S_1 \tag{8}$$

$$2H_{-S_1} \leftrightarrow H_2(g) + 2S_1 \tag{9}$$

Table 2
Kinetic isotopic effects (KIE) of the phenol steam reforming and the water-gas shift reactions studied by SSITKA experiments

| Catalyst | $T$ (°C) | Expt A, $R_{H_2}/R_{D_2}$ | Expt A, $R_{CO_2}$ ($H_2O$)/$R_{CO_2}$ ($D_2O$) | Expt B, $R_{H_2}/R_{D_2}$ |
|---|---|---|---|---|
| 5% Fe/50Mg-50Ce-O | 650 | 0.47 | 0.82 | – |
| | 700 | 0.435 | – | – |
| | 750 | 0.44 | 0.75 | – |
| 0.5% Rh/MgO | 575 | 0.546 | 0.75 | – |
| | 650 | 0.568 | – | – |
| | 755 | 0.541 | 0.78 | – |
| 0.1% Rh/50Mg-25Ce-25Zr-O | 450 | – | – | 0.736 |
| | 600 | – | – | – |
| | 650 | 0.575 | – | 0.75 |
| | 755 | 0.532 | – | – |

SSITKA experiments (2% CO/40% $D_2O$/Ar/He ($T$, $\Delta t$) → 2% CO/40% $H_2O$/Ar ($t$), Expt B) performed in order to follow the H-path of the water-gas shift (WGS) reaction (Eq. (2)) revealed the existence of an inverse KIE for $H_2$ and $CO_2$ formation, as in the case of steam reforming of phenol. Results of the $R_{H_2}/R_{D_2}$ ratio values obtained are reported in Table 2.

The possible contribution of oxygen vacancies or labile oxygen of support during the phenol steam reforming reaction was probed by the following isotopic experiment: 3%$^{18}O_2$/He ($T$, 20 min) → He ($T$, 15 min) → 0.5% $C_6H_5OH$/40% $H_2O$/He ($T$, $t$), Expt C. 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 $^{18}O$ species spilt over from the support to the Rh metal during the reforming reaction (Table 1). However, part of the amount of isotopic $CO_2$ produced during the switch to the phenol/water gas mixture might be the result of the direct exchange of $^{16}O$ atoms of the $CO_2$ molecule with adsorbed $^{18}O$ species (e.g., $C^{16}O_2$ + $^{18}O$-s → $C^{16}O^{18}O$ + $^{16}O$-s). In order to account for this effect, the following experiment had been designed (Expt D): 3%$^{18}O_2$/Ar ($T$, $\Delta t$) → Ar (15 min, 600 °C) → $y$% $CO_2$/40% $H_2O$/Ar (600 °C, $t$). The amount of $^{18}O$ in the CO and $CO_2$ isotopic species produced is reported in Table 1, Expt D. The difference in the amounts of $^{18}O$ between Expts C and D is also reported (Table 1) along with the equivalent amount of $^{18}O$ in terms of surface (Fe or Rh) monolayers, $\theta$. The concentration of $CO_2$ used in Expt D was that measured under steady-state phenol steam reforming reaction conditions. It is noted that under the switch $C_6H_5OH$/$H_2O$ in Expt C this $CO_2$ concentration value is the maximum expected. Therefore, the $^{18}O$ pool expressed in terms of $\theta$ is a lower and not an upper value (Table 1).

Fig. 2 presents transient response curves of $C^{18}O$, $C^{16}O^{18}O$, $C^{18}O_2$ and $C^{16}O$ obtained on the 0.1 wt% Rh/Mg-Ce-Zr-O catalyst following Expt C at 600 °C. The amount of $^{18}O$ appeared in the CO and $CO_2$ gas products (after subtracting the amount measured in Expt D) was found to be 159.5 μmol $^{18}O$/g ($\theta$ = 32.8). It is clear that the major part of $^{18}O$ species was adsorbed on oxygen vacant sites and/or exchanged with labile oxygen of support. This then diffused onto the metal and oxidized the deposited $C_xH_y$ species derived from phenol decomposition [14]. It should be noted that the 50Mg-25Ce-25Zr-O solid consists of $Mg_xZr_{1-x}O_2$ and $Ce_xZr_{1-x}O_2$ solid solution phases [2] that possess significant amounts of oxygen vacant sites. It is reasonable to suggest that these oxygen vacancies and labile oxygen species play a significant role towards decomposition of water. Water can adsorb onto oxygen vacancies of oxidic supports to form labile OH species (Eq. (10)) [15].

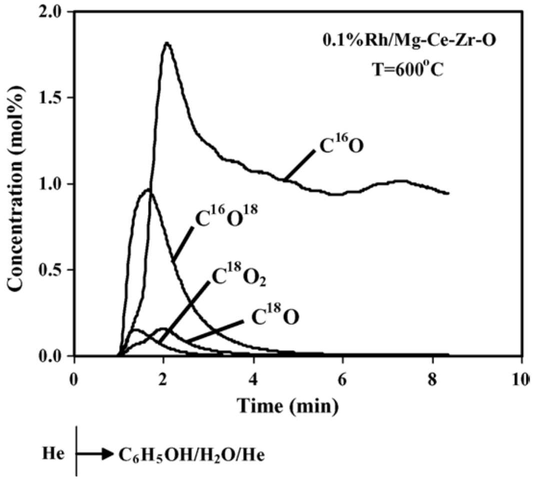

Fig. 2. Transient response curves of $C^{18}O$, $C^{16}O^{18}O$, $C^{18}O_2$ and $C^{16}O$ obtained during Expt C over 0.1 wt% Rh/50Mg-25Ce-25Zr-O catalyst at 600 °C.

$$H_2O\,(g) + O_L + \square_s \rightarrow HO\text{-}\square_s + HO_L \qquad (10)$$

where $\square_s$ is an oxygen vacant site on the support. The latter labile HO-$\square_s$ species are expected to diffuse more easily onto the Rh surface compared to $HO_L$ ones. Therefore, supported-metal catalysts with supports that possess a large amount of oxygen vacancies are expected to highly favor the phenol steam reforming reaction. The latter has already been confirmed in recent studies over supported-Rh catalysts [1,2].

## 4. Conclusions

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

(a) A large pool of active H-containing (H and/or OH) intermediate species residing on the support (Mg-Ce-Zr-O and MgO) participates in the reaction path of steam reforming of phenol to form $H_2$ gas over supported-Rh.
(b) An inverse KIE for the production of $H_2$, CO and $CO_2$ was observed during steam reforming of phenol over Rh/MgO, Rh/Mg-Ce-Zr-O and Fe/Mg-Ce-O.
(c) An inverse KIE for the production of $H_2$ was observed during the water-gas shift reaction over the 0.1% Rh/Mg-Ce-Zr-O catalyst.
(d) Back-spillover of labile OH and O species from the MgO, Mg-Ce-O and Mg-Ce-Zr-O supports to the Rh and Fe metal surfaces was proven by various transient isotopic experiments.

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