Reac Kinet Mech Cat (2011) 104:75–87
DOI 10.1007/s11144-011-0335-y

Ethanol and dimethyl ether steam reforming on Rh/Al_2O_3 catalysts for high-temperature fuel-cell feeds

E. Gucciardi · V. Chiodo · S. Freni · S. Cavallaro · A. Galvagno · J. C. J. Bart

Received: 1 March 2011 / Accepted: 3 June 2011 / Published online: 28 June 2011

Abstract Catalytic reactions of the steam reforming (SR) of dimethyl ether (DME) and (bio)ethanol to hydrogen-rich gas were compared in a fixed-bed continuous-flow reactor at temperatures of 550–650 °C under atmospheric pressure over Rh/Al_2O_3 catalysts in terms of product distribution. Rh/Al_2O_3 catalysts are able to catalyze the high-temperature SR of both EtOH and DME, but in the latter case, higher H_2 yields are obtained and the catalyst is less prone to coking. The aim of this work is to optimise the hydrogen production. Differences in reaction pathways over DME/H_2O and $EtOH/H_2O$ are indicated.

Keywords Steam reforming · Hydrogen · DME · Ethanol · Dimethyl ether

Introduction

Hydrogen is used in industrial activities such as petroleum processing, methanol synthesis, manufacture of fertilizers, annealing of metals and production of electronic materials. New fuel-processing technologies for generating hydrogen tend to be based either on partial oxidation (POX; fast exothermic process) or on steam reforming (SR; endothermic), although the ideal fuel-processor could also function by combining POX and SR [1, 2]. Autothermal reforming (ATR), a particular class of POX processes for converting methane or natural gas to synthesis gas (syngas), includes an exothermic oxidation step and an endothermic SR step in approximate heat balance. However, despite the fact that hydrogen is likely to

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E. Gucciardi · S. Cavallaro (✉) · J. C. J. Bart
Department of Industrial Chemistry and Materials Engineering, University of Messina,
V.le F. Stagno d'Alcontres 31, Sant'Agata di, 98166 Messina, ME, Italy
e-mail: stefano.cavallaro@unime.it

V. Chiodo · S. Freni · A. Galvagno
Istituto CNR-ITAE, Via Salita S. Lucia Sopra Contesse 5, 98126 Messina, ME, Italy

become the most widely used energy carrier of the future, its permanent gaseous nature does neither facilitate storage nor transport. On the other hand, natural fuels and the recently developed synthetic liquids such as biodiesel [3], bioethanol (EtOH) [4], dimethyl ether (DME) [5] and hydrocarbons obtained by Fischer–Tropsch synthesis [6], will also be widely distributed and can be transformed in hydrogen by the aforementioned inverse processes (SR, POX and ATR). In particular, ethanol–water mixtures [7] (bioethanol) and DME [8] are being evaluated nowadays as sources of hydrogen for fuel cell (FC) applications.

The use of chemicals different from hydrogen as feedstocks for FCs has widely been reported [9]. In particular, for high-temperature FCs, several fuels (i.e. methane, methanol, ethanol, higher alcohols, gasoline,…) have been proposed and studied; for low-temperature FCs, mainly methanol has been used, whereas more recently also DME and ethanol have been investigated [10]. The most reported work on SR of DME at low temperature has been carried out using Cu-based catalysts [11–29]. On the other hand, only few studies [28], often of purely theoretical nature [8, 30], have concerned high-temperature SR of DME with only occasionally mentioning the possibility of using non copper-based catalysts. In view of the need for the diversification of feedstocks for mankind's energy needs, it was deemed of interest to evaluate the feasibility of high-temperature SR of DME, in particular in comparison with is isomer EtOH. For this purpose, only few authors have reported the use of a high performance catalyst such as rhodium, which no doubt stands in relation to its cost. However, some advantages are to be gained. Namely, at high temperature, the presence of CO does not represent a problem, and the cogeneration of heat could justify economic performance in particular applications. Therefore, this paper compares the product distribution in SR of EtOH and DME over various Rh-alumina catalysts at high temperatures.

Experimental

Catalyst preparation

Samples have been prepared by supporting the active phase (Rh) on commercial alumina (AKZO-CHEMIE 001-3P) by the wet impregnation technique. Al_2O_3 was first milled and sieved to a size of 40–70 mesh, and then slowly dried and pre-activated at $T = 300$ °C. Afterwards, a weighed amount of this support has been treated with a known amount of a solution containing the active phase precursor $[Rh(NO_3)_3 \cdot nH_2O]$. This procedure has been repeated several times after drying, to reach the prefixed charge of active phase. After impregnation, the system has been calcined at 650 °C for 5 h with a programmed temperature increase of 5 °C/min. Two samples were prepared by this technique, at different Rh loadings: RH02 = 0.2 wt% and RH20 = 2.0 wt% of Rh. A sample named RH00, made of pure alumina, was used as reference.

Characterization techniques

The characterization of the catalytic systems has been carried out by the usual physico-chemical techniques. The amount of charged metal was determined by atomic absorption spectroscopy (PerkinElmer-AAnalyst200). The morphology of the samples was examined by means of TEM observations, made by using a Philips CM12 instrument equipped with a high resolution camera that allows acquisition and evaluation (i.e., of the particle size distribution) of TEM images. Surface areas and pore volumes have been evaluated following the BET methodology by means of a Micromeritics ASAP2010 instrument.

Catalytic tests

Experiments were performed at atmospheric pressure in a fixed-bed linear quartz microreactor ($\Phi_{int} = 4$ mm; $H_{bed} = 1.0$–2.0 cm) charged with 12 mg of catalyst (40–70 mesh) diluted with 200 mg of similar sized inert material (i.e. SiC). Before each test run, catalysts were reduced "in situ" at T = 650 °C for 1 h under flowing hydrogen, and then cooled down to the reaction temperature. For the ethanol SR (SRE), a water/ethanol mixture corresponding to the bioethanol mean composition was fed by an isocratic HP 1100 pump and vaporised at T = 210 °C in a N_2 stream, while for the DME SR, DME and N_2 were fed by a mass flow controller. Experiments were carried out at two different temperature values (550 and 650 °C), gas hourly space velocity (GHSV) = 50,000–200,000 $mL_{fuel}\ h^{-1}\ mL_{cat}^{-1}$ and a steam-to-carbon molar ratio (S/C) of 3 mol/mol. The reaction stream was analyzed online by a Hewlett Packard GC-TCD (model 6890 Plus), equipped with a three-columns (Molecular Sieve 5 Å, Porapak Q and Hysep) system. Nitrogen (10 vol%) was used as an internal standard to evaluate the carbon balance. GC data were acquired and elaborated by the Hewlett-Packard Interface Bus system (HP Chemstation).

The overall amount of coke deposited on the catalytic surface after each test-run has been determined "a posteriori" by CHNS elemental analysis of the discharged sample performed by a Carlo Erba Elementary Analyzer.

For a preliminary evaluation of the thermal reactions for each fuel, blank tests were carried out without catalyst (using only 200 mg of inert material). In all experimental conditions, no differences between inlet and outlet analyses have been detected and just some traces of coke have been found on the discharged SiC under the most stressing conditions (i.e. T = 650 °C and GHSV = 50,000 h^{-1}), when using the EtOH/steam mixture.

Results and discussion

The main characteristic common to the two fuels is their isomericity. Consequently, when vaporized and decomposed, each fuel potentially yields the same amount of H_2 per gas-volume unit, and can be considered a similar hydrogen-storing material. However, due to their different chemical nature and considering their particular logistic availability, from an economical point of view, it can be more or less convenient to use DME or alternatively EtOH. The following investigation examines the reaction pathways of the different fuels, in particular taking into account the effect of temperature on product formation and catalyst life.

Reaction product distribution

Table 1 reports the initial compositions of the stream exiting from the reactor fed with DME/H_2O and EtOH/H_2O mixtures at two temperatures (550 and 650 °C) for GHSV $= 100{,}000\ h^{-1}$. The outlet compositions are qualitatively different for the DME/H_2O and EtOH/H_2O fuels. Whereas several components are commonly observed (e.g. H_2, CO, CH_4, CO_2, H_2O), other products are unique to the specific inlet mixture. In particular, we notice methanol as a reaction product specifically for DME, whereas acetaldehyde and ethylene are formed only from EtOH/H_2O.

Because the main goal of the present study is to optimize the hydrogen production, it is the case to investigate the reaction performance in terms of H_2 yields. Fig. 1 relates the initial amount of hydrogen produced to the experimental parameters playing a role in the conversion of the two fuels (chemical nature, Rh loading and temperature). The hydrogen yield is reported as the ratio between the moles of hydrogen in the outlet and the moles of fuel feed in the inlet. According to the stoichiometric balance (see Eqs. 3 and 4), no more than 6 mol of hydrogen (mol_{H_2}) can be formed from 1 mol of fuel (mol_{Fuel}). The hydrogen yield is maximum for the catalyst with highest Rh content (RH20) and almost zero over pure Al_2O_3. The catalyst with lower Rh loading (RH02) produces a fair amount of H_2 only starting from DME/H_2O, but not from EtOH/H_2O. Anyhow, under the same reaction conditions, DME yields more H_2 than EtOH. A small amount of hydrogen is also produced by pure Al_2O_3 (RH00) for DME/H_2O at high temperature. Under the same reaction conditions, EtOH/H_2O leads to negligible H_2 yields.

Table 1 Outlet selectivity to the typical by-products at $t = 30'$ and coke formation speed

Fuel and catalyst	T (°C)	Outlet composition (vol%)								
		H_2	CH_3CHO	C_2H_4	H_2O	CH_4	CO	CO_2	Fuel	CH_3OH
DME										
RH00	650	7.51	–	–	71.70	1.91	0.20	3.75	5.94	8.98
RH02	650	37.87	–	–	40.84	0.48	5.88	12.66	1.20	1.07
RH20	650	42.14	–	–	37.86	1.69	5.90	10.58	1.82	0.01
RH00	550	0.64	–	–	75.11	0.25	–	0.30	8.99	14.72
RH02	550	11.92	–	–	67.63	0.22	0.32	6.35	6.04	7.52
RH20	550	33.22	–	–	46.14	4.37	2.66	13.02	1.56	0.02
EtOH										
RH00	650	0.57	–	13.22	86.21	–	–	–	–	–
RH02	650	1.22	0.52	13.55	83.61	0.14	–	0.30	0.65	–
RH20	650	42.78	0.06	0.08	35.87	3.45	6.48	10.85	0.43	–
RH00	550	0.20	0.20	12.67	85.53	–	–	–	1.40	–
RH02	550	0.46	–	11.20	85.99	–	–	–	2.35	–
RH20	550	26.37	0.15	–	52.10	6.59	1.65	11.52	1.61	–

S/C molar ratio = 3

RH00 pure alumina, *RH02* Rh (0.2 wt%) supported on Al_2O_3, *RH20* Rh (2.0 wt%) supported on Al_2O_3

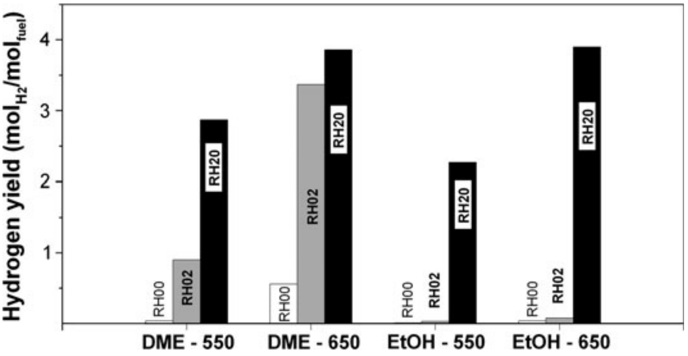

Fig. 1 Initial yields of hydrogen (mol_{H_2}/mol_{fuel}) from DME/H_2O and EtOH/H_2O at two temperatures (550 and 650 °C)

The SR of DME is a two-step process including DME hydration to methanol (Eq. 1) and SR of methanol (SRM) to hydrogen-rich gas (Eq. 2):

$$CH_3OCH_3 + H_2O \leftrightarrows 2CH_3OH \quad \Delta H_r^0 = 36.6\,kJ\,mol^{-1} \tag{1}$$

$$CH_3OH + H_2O \leftrightarrows 3H_2 + CO_2 \quad \Delta H_r^0 = 49.1\,kJ\,mol^{-1} \tag{2}$$

Overall:

$$CH_3OCH_3 + 3H_2O \leftrightarrows 6H_2 + 2CO_2 \quad \Delta H_r^0 = 135.0\,kJ\,mol^{-1} \tag{3}$$

Thanks to this mechanism, DME readily and selectively converts to hydrogen-rich gas at rather low temperatures (250–350 °C) [11] and several studies have been carried out directed to work at the lowest possible temperature (i.e. mainly for automotive FC applications—*cfr.* Table 2).

The hydrolysis of DME, the limiting step in the overall SRDME process, is equilibrium controlled and limited by a low equilibrium constant (with equilibrium conversion of DME at 200 °C being 15%) when carried out without the removal of the methanol produced. SRDME activity strongly depends on the acidic catalyst that is active for DME hydrolysis. Not only the amount of acidic catalyst, but also the acid strength and type of acid site affect the SR and hydrolysis activity [25]. Stronger acidity gives higher DME hydrolysis conversion [29]. Strong acids allow for high SRDME activity at low temperatures (200–275 °C), while weak Lewis acid sites of alumina require higher temperatures (at least 275–450 °C). CO_2 and CO with relatively small amounts of CH_4 are observed as primary carbon-containing compounds when alumina is used as the acidic catalyst.

SRM over Cu/ZnO/Al_2O_3 has been explained in terms of methanol dehydrogenation, methyl formate hydrolysis and formic acid decomposition [31]. Hydrogen production depends significantly on temperature and space velocity.

SRE is often carried out with mono-, bi- or tri-metallic supported catalysts [4, 32–35] to produce H_2 and CO_2 according with the overall thermodynamic equation:

Table 2 Composite DME hydrolysis and SR catalysts

Acidic species	Reforming species	T_r (°C)	Reference
γ-Al_2O_3	Cu, Zn	350–500	[15]
Al_2O_3, SiO_2, Al_2O_3	Cu, Fe, Co, Pd, Ir, Pt, Rh, Ni	250–400	[16]
ZrO_2, CeO_2/ZrO_2	Pt, Rh[a]	370–540	[2]
γ-Al_2O_3	HPA[b] + Cu/SiO_2	200–360	[17]
γ-Al_2O_3, SiO_2	Cu, Cu–Zn	200–500	[18]
H-mordenite, SO_4^{2-}/ZrO_2, WO_3/ZrO_2	Cu/CeO_2	200–350	[19]
Zeolite A, mordenite, ferrierite	Pt, Ru, Pd, Rh, Ir, Cr, Co, Ni, Cu, Fe, Sn	300–500	[20]
γ-Al_2O_3	$Cu/ZnO/Al_2O_3$, CuB_2O_4 (spinels) (B = Mn, Al, Fe, Cr)	250–450	[21]
Al_2O_3, Ga_2O_3, Ga_2O_3–Al_2O_3	Cu	200–400	[22]
Al_2O_3	Cu/Zn	n.a.	[23]
Zeolite Y, ZSM-5, ZrO_2, γ-Al_2O_3	Cu/Zn	125–400	[24]
ZSM-5	$Cu/ZnO/Al_2O_3$	200–400	[25]
Zeolite Y, ZSM-5, ZrO_2, γ-Al_2O_3	$Cu/ZnO/Al_2O_3$	125–400	[26]
Al_2O_3, ZrO_2, CeO_2, TiO_2	Pt, Pd, Ir, Rh, Ru	200–400	[27]
H-mordenite, ZSM-5, Al_2O_3	$CuFe_2O_4$	200–450	[28]
Al_2O_3	$CuFe_2O_4$	250–450	[29]
–	Ce–ZrO_2	900	[31]
WO_3/ZrO_2	$CuZnAlO_x$	200–320	[32]
α-Al_2O_3	CuO–CeO_2	250–370	[33]
γ-Al_2O_3, ZSM-5	CuO–ZnO–Al_2O_3–ZrO_2	200–400	[34]

[a] Combination of POX and SR

[b] *HPA* 12-tungstosilicoheteropolyacid ($H_4SiW_{12}O_{40}$)

$$CH_3CH_2OH + 3H_2O \leftrightarrows 6\,H_2 + 2CO_2 \quad \Delta H_r^0 = 207.7\,kJ\,mol^{-1} \tag{4}$$

According to the most commonly accepted mechanism [35], the initial reaction steps are represented by the two parallel reaction pathways:

$$CH_3CH_2OH \leftrightarrows C_2H_4 + H_2O\,(\text{dehydration}) \tag{5}$$

and

$$CH_3CH_2OH \leftrightarrows CH_3CHO + H_2\,(\text{dehydrogenation}) \tag{6}$$

Subsequently, the end products (CH_4, CO, CO_2, H_2, coke,…) are formed as follows:

$$n\,C_2H_4 \leftrightarrows (C_2H_4)_n \rightarrow H_2 + C_{(s)}\,(\text{coking}) \tag{7}$$

$$CH_3CHO \rightarrow CH_4 + CO \tag{8}$$

$$CH_4 + H_2O \leftrightarrows CO + 3\,H_2 \tag{9}$$

$$CO + H_2O \leftrightarrows CO_2 + H_2 \tag{10}$$

Influence of contact time and Rh concentration

Fig. 2 shows the outlet composition as a function of the spatial velocity of the fuel (DME or EtOH). The remainder of the mixture mainly consists of excess steam, non-converted fuel (DME or EtOH) and specific intermediate reaction products (acetaldehyde, ethylene, methanol). As discussed before, acetaldehyde and, in particular, ethylene are formed in appreciable amounts (10–20 vol%) using EtOH/steam mixtures over low Rh content catalysts. Under similar circumstances, SR of DME produces discrete quantities of methanol (0–10 vol%). The catalyst used for the experiments in Fig. 2, with the highest Rh concentration (RH20—2 wt%), leads to an almost total conversion of the intermediates to CH_4, CO_x and H_2, while the outlet concentration of C_2 or MeOH does not exceed 1 vol%.

Irrespective of the starting fuel (EtOH or DME), and at variance to earlier findings [36, 37], none of our experiments confirmed a total absence of coke. In the temperature range of interest, the acidity of alumina favors the formation of carbocations and unsaturated hydrocarbons, which are precursors to coke formation. A high Rh loading (i.e. 2 wt%) catalyzes the Boudouard reaction and produces CO_2 and coke from the initially produced CO:

$$2\,CO \leftrightarrows CO_2 + C_{(s)} \tag{11}$$

As a result of the two different reaction mechanisms, the morphology of the carbonaceous residues is highly variable, and it is difficult to correlate the quality of coke with the operating variable parameters (T, p, GHSV, t,…). In fact, a greater quantity of coke formed initially could well correspond to a smaller particle size, resulting in more favorable mechanical transport by the gas stream. As a result, the quantity of coke determined on the used catalyst is lower than formed effectively.

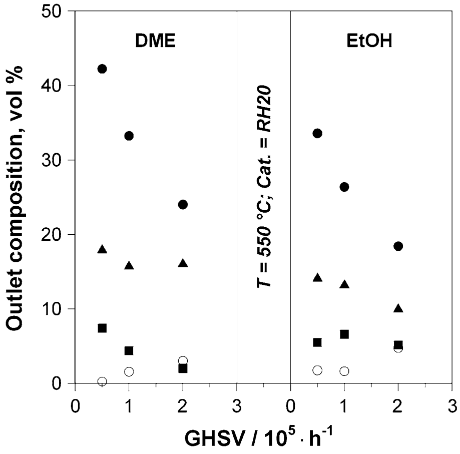

Fig. 2 Outlet composition (vol%) versus inlet fuel GHSV (h^{-1}). Reaction temperature T = 550 °C; catalyst Rh–2 wt%/Al_2O_3 (i.e. RH20): *filled circles* hydrogen; *filled squares* methane; *open circles* unconverted fuel; *filled triangles* carbon oxides ($CO + CO_2$). Unreported: methanol, internal standard (i.e. N_2) and C2 products (i.e. ethylene and/or acetaldehyde)

Catalyst decay

Fig. 3 shows the conversions of DME and EtOH as a function of time on stream. All catalysts maintain their initial activity at short run, except for RH20, which decays rapidly in SRE at 550 °C. As to the SRE, a less pronounced gradual decrease in activity was also noticed at 650 °C, whereas the catalytic activity over DME was more stable, even up to a certain reactivation with time. This anomalous behavior can be explained by ascribing the decay to deposition of coke on the reactive sites and to the fact that the total "conversion" is the result of various simultaneous serial/parallel reactions. Depending on the catalytic site affected, a certain reaction may be blocked and/or promoted by coking. Anyhow, in accordance with its chemical nature, experimentally, ethanol turns out to be less stable than DME and the observed higher coke formation tendency (see Table 1; Fig. 4) is accompanied by a more rapid decrease in conversion, despite the absence of a precise correlation. Only Rh containing catalysts (RH02 and RH20) decay, with the coke formation rate being highest for the catalyst with the lowest Rh concentration (RH02). This can be rationalized by admitting the presence of two different simultaneous mechanisms for coking. In the absence of Rh (i.e. RH00, or pure-alumina) the catalytic activity over a great number of surface sites is low and the mechanism involved is predominantly acidic in nature. The initial protonation of the hydroxyl is followed by the dehydration with the formation of a double bond and subsequent polymerization. In the presence of small amounts of Rh, disproportionation of CO (Boudouard reaction) with formation of CO_2 and coke (Eq. 11) may also occur.

In analogy to the observations for the conversions, the H_2 yield (Fig. 5) is relatively constant for all catalysts at low or zero Rh concentration (RH02 and

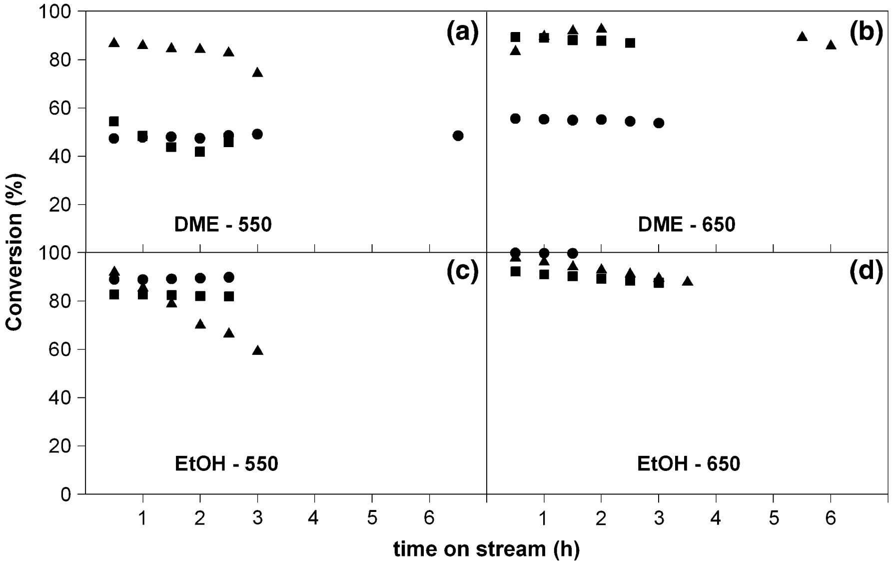

Fig. 3 Conversions of DME and EtOH as a function of time on stream at two temperatures (550 and 650 °C): *filled circles* RH00; *filled squares* RH02; *filled triangles* RH20

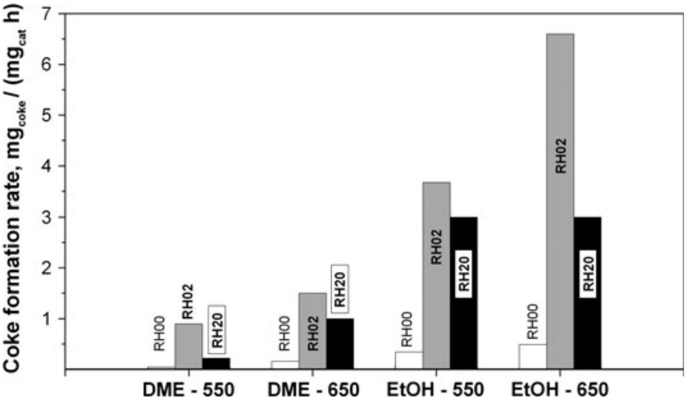

Fig. 4 Coke formation rate ($mg_{coke}\ g_{cat}^{-1}\ h^{-1}$) on different catalysts. General conditions: T = 550, 650 °C; GHSV = 100,000 h^{-1}; S/C ratio = 3 mol/mol; fuels = DME, EtOH

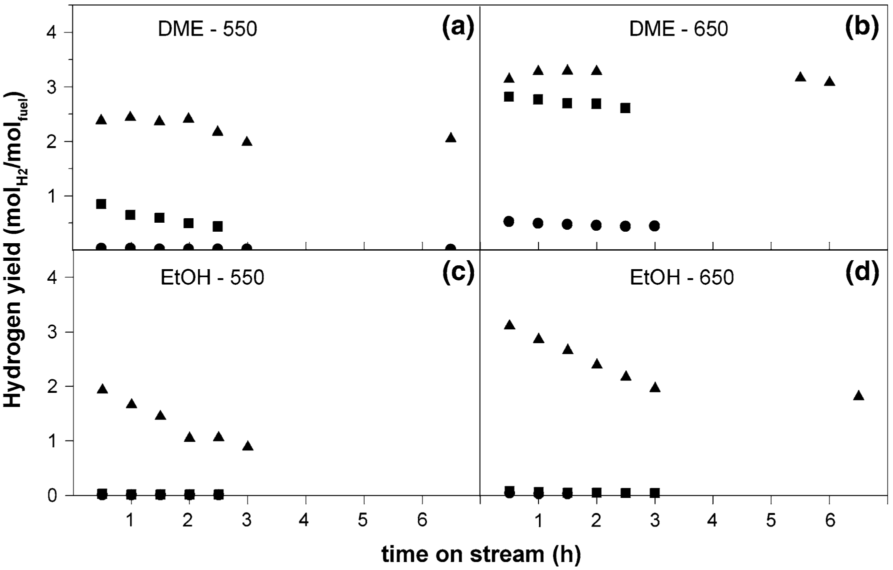

Fig. 5 Hydrogen yields (mol_{H_2}/mol_{fuel}) for DME/H_2O and EtOH/H_2O as a function of time on stream for two temperatures (550 and 650 °C): *filled circles* RH00; *filled squares* RH02; *filled triangles* RH20

RH00, respectively) in the case of DME/H_2O, whereas the yield in hydrogen decreases rather rapidly with time on stream for the 2 wt% Rh/Al_2O_3 catalyst (RH20) fed with EtOH/H_2O, both at 550 and 650 °C.

Reaction pathways

The complex reaction pathway can be more easily understood if we start from the basic chemical nature of the three catalysts. Various composite catalysts, either bifunctional or mechanical mixtures of two components, consisting of a solid acid for DME hydration and a metal catalyst for SRM, have recently been reported in the scientific literature for SRDME (Table 2). Special attention is needed for designing a SRDME catalyst since the proper distribution of acidic as well as reforming species (usually metals such as Cu, Pd or Pt) is very important to perform the hydrolysis and reforming reactions in a synergistic manner. Catalytic generation of hydrogen by SRDME for FC applications has also been object to several patents [2, 12, 13, 17]. SRDME has been considered for both MCFCs [10] and PEFCs for stationary and automotive applications [20]. Our bifunctional catalysts are made by Rh supported on alumina, and the (de-)hydrogenating function competes to Rh, while the acidic function is represented by the Lewis sites of alumina. The same composite material was used in the past [38, 39] to study similar complex reactions.

The pure alumina support (RH00), used as a blank and working as a Lewis acid, promotes DME hydrolysis (see Eq. 1), cracking of hydrocarbons and dehydration of alcohols. It does not produce hydrogen by dehydrogenation or SR reactions, but a small amount of H_2 can be produced by CH_4 pyrolysis at high temperature. Methane is a stable molecule and can be cracked by RH00 only at 650 °C (see Fig. 1). On the other hand, as reported in Table 1, ethylene can be formed by dehydration of EtOH (Eq. 5) and methanol is formed by DME hydrolysis (Eq. 1). Ethylene can represent the first step of coking as observed on all RH00 discharged catalysts (*cfr*. Table 1), but yields are very low because of low surface area (i.e. 243 m^2/g). However, as DME hydrolysis represents the first reaction step of SRDME, the presence of alumina is needed in the catalyst composition [40].

The Rh loading enhances H_2 production, mainly at high temperature and by using DME. As reported in Figs. 3a, b and 5a, b both the conversion and the hydrogen yield are almost constant as a function of time on stream and a 96% conversion and H_2 yield of approximately 40% of the theoretical value were reached for the RH20 sample at $T = 650$ °C. A different situation was observed in using ethanol as a feed (Figs. 3c, d, 5c, d), where fast catalyst decay was recorded. In fact, the enhanced coke formation (see Table 1) due to dehydration of ethanol strongly favors the shell encapsulation of the active phase (Rh crystallites) and fast catalyst poisoning. TEM micrographs reported in Fig. 6 confirm this hypothesis. In any case, for higher fuel conversions (at higher temperature or Rh loadings), coking is more pronounced and a homogeneous soot distribution on the catalytic surface was observed.

Only small traces of CO or CO_2 can be detected on pure alumina (RH00) or on a low-charged catalyst (RH02), while both carbon oxides were detected for RH20. Considering that similar selectivities are expected for the same mechanism, and that Rh catalyzes all the hydrogen-involving reactions, a change of selectivity in terms of CO_2/CO ratio could denote a different mechanism. In effect, the same behavior of the reaction was detected using DME or EtOH as a hydrogen source (Fig. 7) and a change in reaction pathway is therefore unlikely. Moreover, in contrast to thermodynamic expectations [10], CO_2 increases with temperature for all reaction conditions examined, while CO_2/CO always decreases upon poisoning. This can be rationalized by a rate determining step involving CO oxidation by the water gas shift (WGS) reaction (Eq. 10).

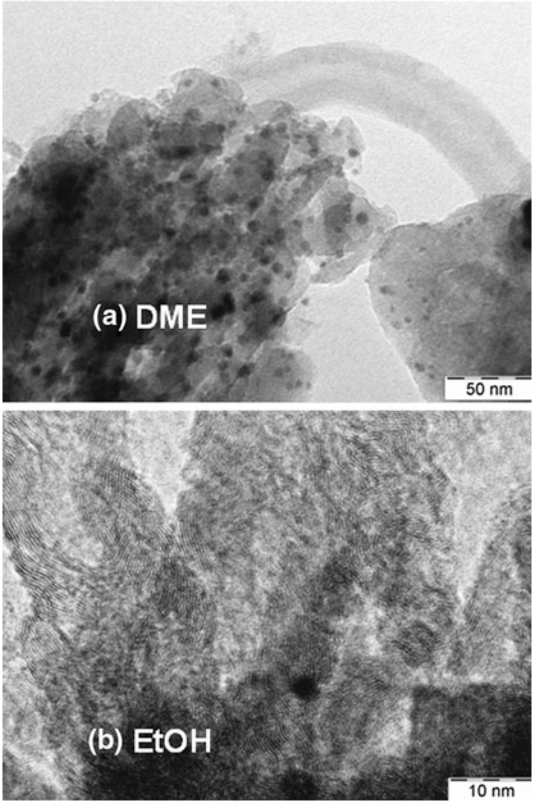

Fig. 6 TEM micrographs of the RH02 catalytic system discharged after use in DME (**a**) and EtOH (**b**) SR. Carbon "whiskers" and "shell-encapsulated" Rh sites are shown, respectively

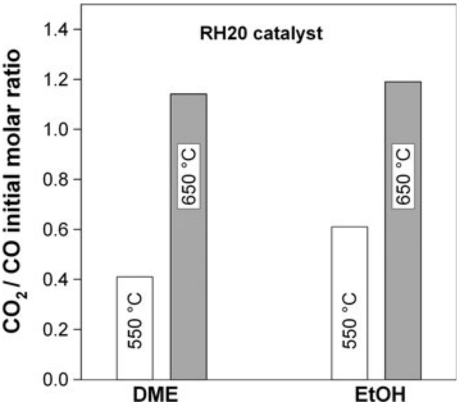

Fig. 7 CO_2/CO initial molar ratio as a function of fuel (DME or EtOH) and temperature for the RH20 (2 wt%) catalyst

Conclusions

Rh/Al_2O_3 catalysts are able to catalyze SR of both EtOH and DME. In accordance with the previous literature, the reaction pathways differ leading to different by-products. While DME needs a first step on acid sites (hydrolysis to methanol) and a second one by a hydrogenating supported metal (SRM on Rh crystallites), the presence of acid sites is undesired for ethanol. Dehydrogenation of the substrate and the consequent ethylene formation, in fact, strongly favor coke formation and decrease catalyst life time. The catalyst with lower Rh loading (RH02) produces a fair amount of H_2 only starting from DME/H_2O, as opposed to EtOH/H_2O. Formation of CO and CO_2 is inhibited by poisoning of Rh by coking; at higher temperatures more CO_2 than CO is formed. Because of the above, in comparison to EtOH high-temperature SR of DME leads to higher H_2 yields and is less prone to catalyst coking. In process kinetics, the water gas shift plays an important role and very short contact times together with a very active catalyst (i.e. Rh) can be used.

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