Catalysis Today 143 (2009) 2–8

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Hydrogen from alcohols: IR and flow reactor studies

Guido Busca [a,*], Tania Montanari [a], Carlo Resini [a], Gianguido Ramis [a], Umberto Costantino [b]

[a] Dipartimento di Ingegneria Chimica e di Processo, Università di Genova, Genova, Italy
[b] CEMIN, Centro di Eccellenza sui Materiali Innovativi Nanostrutturati, Dipartimento di Chimica, Università di Perugia, I-06100 Perugia, Italy

ARTICLE INFO

Article history:
Available online 1 November 2008

Keywords:
Hydrogen productions
Renewable sources
Steam reforming
Ethanol steam reforming
Methanol steam reforming
Alcohol steam reforming

ABSTRACT

The reactions of methanol and ethanol steam reforming (MSR and ESR) have been studied over Cu-ZnO-Al_2O_3 and over Ni-containing catalysts, respectively. Our spectroscopic studies, coupled with flow reactor studies, allowed us to propose mechanisms for both reactions where water takes the role of oxidant of part of the copper and nickel species. The uncompletely reduced catalysts convert the alcohols into formate and acetate species, respectively, plus gas phase hydrogen. Over Cu-ZnO-Al_2O_3 formates decompose into adsorbed CO which is rapidly oxidized into CO_2 before leaving the surface. This allows CO production lower than forecast from the WGS equilibrium. Over Ni-based catalysts acetates decompose into CO and methane. In fact, the ESR reaction was found to produce, above 700 K, hydrogen, carbon oxides and methane. The formation of hydrogen is limited by the establishing of the WGS (which would likely unavoidably limit the one-step production of hydrogen by ESR) and the methane SR equilibria. Activation of the C2 carbon atom of ethanol or of some of its decomposition products would be needed to avoid methane formation, thus increasing hydrogen yield.

Preliminary work on isopropanol SR was performed over a Pd-Cu catalyst. Cracking and production of methane lower significantly the selectivity to COx and hydrogen.

1. Introduction

Hydrogen is an energy carrier which, coupled with the use of fuel cells (FC) and electric engines, could allow an efficient and environmental friendly management of the energy resources. An excellent review concerning the processes allowing hydrogen production from carbon feedstocks has been published recently by Navarro et al. [1]. This work summarizes not only the excellent work done in this field by the group of J.L. Garcia Fierro and his coworkers, but also the international literature in the subject. The large scale industrial production of hydrogen is based today on methane or natural gas steam reforming (SR), mostly performed on Ni-$MgAl_2O_4$ based catalysts in the range 900–1200 K [1,2]. Actually, to complete hydrogen production and allow easier purification of hydrogen from CO_x, the water gas shift reaction should be performed in one or more later steps, coming to its equilibrium position at the lowest possible temperature (usually 470–520 K). CO_2 is co-produced during these processes, separated and mostly vent, thus increasing the greenhouse gas concentration in the atmosphere. Technical and environmental problems also arise from the need to develop efficient technologies for hydrogen storage and distribution.

The uses of alcohols as hydrogen sources may allow, in spite of their much higher prices, to partially solve these problems. Methanol is in fact a relatively cheap liquid with high hydrogen content that can allow the production of hydrogen with a much less endothermic process, working at much lower temperature (550–750 K) [3]. Methanol has been produced in the past by wood pyrolysis and may be synthesized from syngases produced by biomass gasification. Thus, the use of “bio-methanol” would potentially avoid to increase the greenhouse gas concentration in the atmosphere. Small scale hydrogen production as well as on-board production of hydrogen in fuel-cell/electric engine vehicles can be performed using methanol, using catalysts based on Cu-ZnO/Al_2O_3.[4].

“Bioethanol”, i.e. ethanol produced from glucose-rich biomasses, is an already available renewable liquid fuel and allows the production of hydrogen by SR [5–8]. Ethanol SR is thermodynamically feasible at intermediate temperature, thus possibly also giving some process advantage with respect to SR of methane. Other alcohols may be produced from biomasses through chemical or biotechnological processes and may be taken into consideration as renewable sources of hydrogen.

---

[*] Corresponding author. Tel.: +39 0103 536024; fax: +39 0103 536028.
E-mail address: Guido.Busca@unige.it (G. Busca).

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.09.010

While methane steam reforming (MeSR) is a well established technology [1,2], and methanol SR (MSR) has also been already developed at the industrial level [9], ethanol SR (ESR) is still at the development stage, the formulation of the best catalyst being still under debate. To develop the best catalysts and to improve process performances, the knowledge of reaction pathways and mechanisms is crucial. For MSR, the sequence of production of the main C-containing product CO_2 and of the main byproduct CO, as well as the possible role of formic acid as an intermediate have been the object of discussion. The reaction pathway for ESR is even more complicated, the mechanism of formation of the main byproduct, methane, being still matter of debate. In our laboratories, investigations have been undertaken to develop new catalysts for these processes and to improve the knowledge of the mechanisms of the processes allowing the production of hydrogen.

2. Experimental

2.1. Catalytic activity tests

The catalytic tests were conducted in a fixed bed quartz tubular flow reactor. Product analysis was performed with an on-line gas-chromatograph (GC) in order to detect both carbon species and H_2. The gas-chromatograph employed was an Agilent 4890 GC equipped with a Varian capillary column “Select Permanent Gases Molsieve 5A/Porabond Q Tandem” and TCD and FID detectors in series. Between them a Nickel Catalyst Tube has been employed to reduce CO to CH_4. A six-port valve with a 0.5 cm^3 loop was used for the gas sampling of the outlet gases.

The MSR experiments reported here were performed with a bed containing 44 mg of catalyst dispersed into 450 mg of quartz (both of them 60–70 mesh sieved). The gas feed was constituted by CH_3OH: 4.5%; H_2O: 5.0%; He balance. Experiments were performed at total flow: 80 ml/min, corresponding to a contact time $\tau = 0.033$ s, and total flow: 320 ml/min, $\tau = 0.0082$ s.

For ESR catalytic experiments discussed here two conditions have been used: (a) the reactor loaded with 25 mg of catalyst mixed with 275 mg of quartz particles (both of them 60–70 mesh sieved), total feed rate was 125 ml/min, with the composition: 63.4% N_2, 9.2% C_2H_5OH and 27.4% H_2O (i.e. water to ethanol ratio 3) or, (b) catalyst weight 15 mg, total feed rate was 300 ml/min; water to ethanol ratio 6.

Results are reported based on reactants conversion and products selectivities defined as usual. The hydrogen yield has been alternatively defined as follows.

$$Y_{H2} = \frac{\boldsymbol{n}_{\mathrm{H2prod}}}{\boldsymbol{n}_{\mathrm{ROHin}}}$$

i.e. as the molar ratio from hydrogen in products and alcohol in the feed. Thus 100% hydrogen yield corresponds to 3 for MSR and 6 for ESR.

2.2. Infrared studies

In situ IR studies have been performed using Nicolet FT-IR spectrometers and home made pyrex glass cells and vacuum/gas manipulation lines allowing the pretreatment of the catalyst disk, the feed of gases and vapours at different temperatures and the analysis of the surface species as well as of the gas phase in the transmission/absorption mode.

2.3. Catalysts preparation

Cu-Zn-Al catalysts for MSR and Ni(Co)-Zn-Al and Ni-Mg-Al catalysts for ESR have been prepared by calcining hydrotalcite layered double hydroxide like precursors [10]. The other catalysts have been prepared by conventional impregnation procedures.

3. Results and discussion

3.1. Thermodynamic considerations

MSR to CO_2 and hydrogen is a weakly endothermic reaction that can be performed in relatively mild conditions, being thermodynamically favored ($\Delta G^\circ < 0$) already at room temperature:

$$CH_3OH + H_2O \leftrightarrows CO_2 + 3H_2, \quad \Delta H^\circ_{298} = +49.5\,\mathrm{kJ/mol}, \quad \Delta S^\circ_{298} = +177\,\mathrm{J/K\,mol}, \ \Delta G^\circ_{298} = -3\,\mathrm{kJ/mol}$$

Formally, MSR could be assumed to be the sequence of methanol decomposition, which is even more endothermic, and the slightly exothermic water gas shift (WGS) reaction:

$$CH_3OH \leftrightarrows CO + 2H_2, \quad \Delta H^\circ_{298} = +90.6\,\mathrm{kJ/mol}, \quad \Delta S^\circ_{298} = +219\,\mathrm{J/Kmol}, \quad \Delta G^\circ_{298} = +25.3\,\mathrm{kJ/mol}, \quad \Delta G^\circ = 0 \text{ at } \sim 410\,\mathrm{K}$$

$$CO + H_2O \leftrightarrows CO_2 + H_2, \ \Delta H^\circ_{298} = -41\,\mathrm{kJ/mol}, \quad \Delta S^\circ_{298} = -42\,\mathrm{J/K\,mol}, \ \Delta G^\circ_{298} = -29\,\mathrm{kJ/mol}, \quad \Delta G^\circ = 0 \text{ at } \sim 1100\,\mathrm{K}$$

It can be noted that, in the conditions where methanol decomposition starts to be favored ($\Delta G^\circ < 0$), still WGS is favored too and allows to shift to right the methanol decomposition equilibrium. Also, this allows low CO and high CO_2 concentrations being obtained, thus possibly avoiding the need of a separate WGS step.

ESR is definitely more endothermic than MSR, but less than MeSR:

$$C2H5OH_g + H2O_g \leftrightarrows 2CO + 4H_2, \quad \Delta H^\circ 298 = +256\,\mathrm{kJ/mol}, \quad \Delta S^\circ 298 = +448\,\mathrm{J/K\,mol}, \quad \Delta G^\circ 298 = +122.5\,\mathrm{kJ/mol}, \quad \Delta G^\circ = 0 \text{ at } \sim 573\,\mathrm{K}$$

$$C2H5OH_g + 3H2O_g \leftrightarrows 2CO2 + 6H2, \quad \Delta H^\circ_{298} = +174\,\mathrm{kJ/mol}, \quad \Delta S^\circ_{298} = +364\,\mathrm{J/K\,mol}, \quad \Delta G^\circ_{298} = +65.5\,\mathrm{kJ/mol}, \quad \Delta G^\circ = 0 \text{ at } \sim 483\,\mathrm{K}$$

ESR starts to be favored at temperatures at which WGS is still but less favored and is frequently performed at even higher temperatures. For these reasons, a further low temperature WGS step might be necessary to complete hydrogen production and CO_2 formation after ESR.

Even more endothermic is conversion of higher alcohols such as 2-propanol into carbon oxides and water. However, due to the higher value of increase of enthropy, the temperature for SR of higher alcohols to become favored may be lower:

$$iC3H7OH_g + 2H2O_g \leftrightarrows 3CO + 6H2, \quad \Delta H^\circ 298 = +424\,\mathrm{kJ/mol}$$

3.2. MSR over Cu-ZnO-Al_2O_3 catalysts

The results of MSR at two different contact times over a catalyst with composition Cu:Zn:Al a.r. 45:31:23 are shown in Fig. 1. It is evident that conversion is strongly accelerated at higher contact times, being total at 623 K and producing almost exclusively the MSR reaction with extremely high selectivities. The formation of other oxygenates and of CO is almost zero in our conditions. As discussed elsewhere, the effect of copper loading is not very high, excellent conversion being also obtained with a catalyst with Cu: Zn:Al ratios of 18:33:49 [3] and also with a catalyst with Cu: Zn:Al ratios of 5:52:43 [11]. Additionally, it has been shown that, when methanol only is fed to the catalyst, the decomposition reaction is definitely slower than MSR and gives rise to pure CO and hydrogen, with essentially no CO_2 [3]. Interestingly, the CO/CO_2 ratio in the products of MSR is, taking into consideration also the hydrogen and water partial pressure in the products, definitely lower than that expected from the thermodynamics of the WGS equilibrium. This indicates that MSR is not a sequence of methanol decomposition and WGS. Small amounts of CO can either be produced by the reverse WGS (i.e. from the reaction of the MSR products CO_2 and H_2) or by a parallel path.

Infrared studies have been performed in order to elucidate the mechansim of this reaction.

To provide evidence for the role of water, three different catalyst pretreatments have been performed: (i) simple outgassing at 723 K; (ii) reduction in hydrogen at 723 K and outgassing at 723 K; (iii) reduction in hydrogen at 723 K, treatment with water at 523 K, and final outgassing at 523 K.

The difference between the spectra observed after pretrements (i) and (ii) is a strong band at 1030 cm^{-1}, which has already been found after hydrogenation of $Cu\text{-}ZnO\text{-}Cr_2O_3$ catalysts [12] and assigned to adsorbed hydrogen bridging over more copper atoms. This is typical of the reduced state of the catalyst after pretreatment (ii).

The IR spectra of the surface species observed after interaction of the catalyst after the three pretreatments with methanol at 523 K are compared in Fig. 2. It is evident that the surface species after pretreatment (i) and after pretreatment (iii) are closely similar, while those observed after pretreatment (ii) are different. This strongly suggests that water is able to partially reoxidize the catalyst to a redox state which is similar to that of the catalyst after simple outgassing at 723 K.

The adsorption of methanol over the catalyst after pretreatments (i) and (iii) gives rise to a mixture of methoxy (C–O stretchings/CH_3 rocking at 1083 and 1027 cm^{-1}, CH_3 deformations at 1467, 1452 cm^{-1}) and at least two kinds of formate groups (COO asym stretching modes at 1610 and 1597 cm^{-1}, CH deformation at 1392 cm^{-1}, COO symmetric stretching at 1375 cm^{-1}). The analysis of the spectra shows that methoxy groups convert into formate species with the possible intermediacy of dioxymethylene species, the adsorbed form of formaldehyde [13], finally giving rise to carbon oxides.

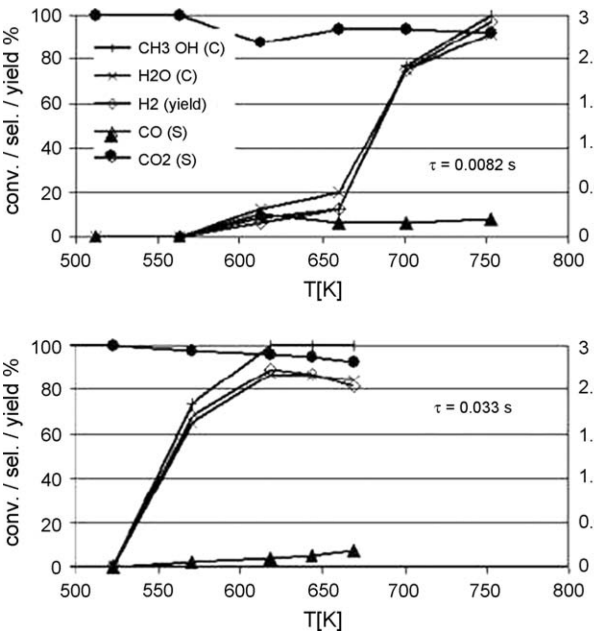

Fig. 1. Conversion of methanol and selectivities and yields for MSR with two different contact times over $Cu\text{-}ZnO\text{-}Al_2O_3$ catalyst.

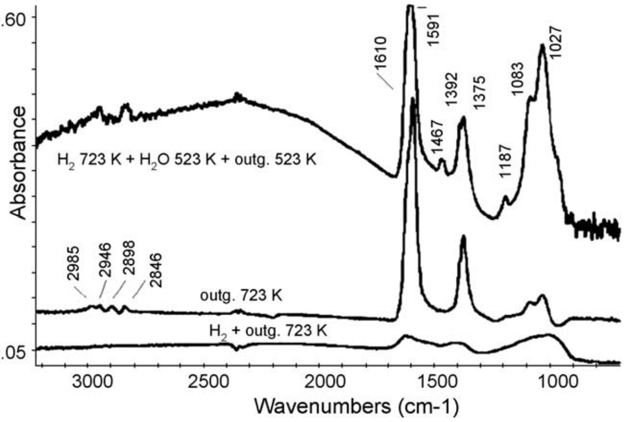

Fig. 2. FT-IR spectra of the adsorbed species arising from the contact of the $Cu\text{-}ZnO\text{-}Al_2O_3$ catalyst after three different pretreatments with methanol vapor at 523 K.

The state of the surface copper sites may be probed by IR of adsorbed CO. It is well known that CO adsorbs strongly on Cu^+ centers, giving rise to bands in the region 2140–2100 cm^{-1}, while adsorption of CO on Cu° gives rise to very weakly bonded carbonyls absorbing in the 2100–2050 cm^{-1} range. CO adsorbs at low temperature also on Cu^{2+} sites, but, upon warming, these species disappear producing carbon dioxide [14–16]. It has been shown that, by increasing the outgassing time or temperature, the catalyst slightly reduces with the increase of the amount of Cu° centers [17]. IR spectra show that CO adsorbed on the unreduced or uncompletely reduced catalyst gives rise to CO_2 formation at very mild conditions. This is shown in Fig. 3 where the formation of adsorbed CO_2 (strong band at 2340 cm^{-1}) is evident during warming from 130 to 170 K upon outgassing (spectra 2–4) after CO adsorption at 130 K, with the parallel shift of the band of copper carbonyls toward a lower frequency (2115 cm^{-1}, spectrum 6), due to the superposition of the band of Cu^+–CO with that of Cu°–CO. The peak at 2190 cm^{-1}, shifting to higher frequency by outgassing, is attributed to CO adsorbed on Al^{3+} ions, while the peak at 2161 cm^{-1} is likely due to CO adsorbed on both Cu^{2+} and Zn^{2+}.

These data allowed us to conclude [18] that the likely mechanism of MSR is that reported in Scheme 1. Methoxy groups (i.e. dissociatively adsorbed methanol) give rise to dioxymethylene and formate groups that decompose to CO. When the catalyst is in the presence of water, a high concentration of oxidized Cu^{2+} and Cu^+ centers exist. CO is retained on the surface and oxidized to CO_2 before leaving the surface so escaping the WGS equilibrium. Water reoxidizes Cu centers which are reduced during the process.

3.3. ESR over Ni-containing catalysts

Ethanol SR has been investigated over Ni and Ni–Co alloys supported on yttria stabilized zirconia (YSZ) [19] as well as over $Ni(Co)\text{-}ZnO\text{-}Al_2O_3$ and $Ni\text{-}MgO\text{-}Al_2O_3$ catalysts obtained by calcination of hydrotalcite-like precursors.

In Fig. 4 the behavior of Ni and Ni–Co alloys supported on YSZ are compared in the medium temperature range (conditions (a) in the experimental section). Below 700 K different organic products, such as ethylene, diethylether, acetic acid and acetaldehyde are formed. In all cases total conversion of ethanol is reached above 700 K. The yield in hydrogen is limited by the formation methane and of CO instead of CO_2. However, Ni–Co alloy allows a better

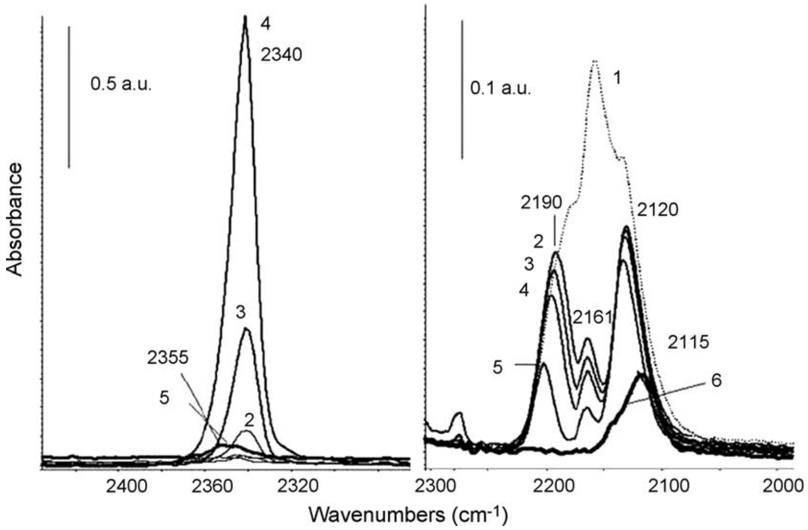

Fig. 3. FT-IR spectra of CO adsorbed at 130 K (spectrum 1) and after outgassing at 130 K (2), 150 K (3), 170 K (4) and 190 K (5) on Cu-ZnO-Al_2O_3 catalys,t pretreated by reduction in hydrogen at 723 K and treatment with water at 523 K and following outgassing at 523 K.

Dissociative adsorption of methanol / decomposition of methoxy groups into formate groups

$CH_3OH_g + 2\,O^{2-}{}_{surf} \leftrightarrows CH_3O^-{}_{surf} + {}^-OH_{surf} + O^{2-}{}_{surf} \leftrightarrows HCOO^-{}_{surf} + {}^-OH_{surf} + H_{2\,g} + 2e^-$

Decomposition of formate groups into CO_2.

$HCOO^-{}_{surf} + {}^-OH_{surf} \rightarrow CO_{surf} + 2\,{}^-OH_{surf} \rightarrow CO_{2\,g} + H_{2\,g} + O^{2-}{}_{surf}$

Reoxidation of the surface by water

$H_2O_g + 2e^- \leftrightarrows H_{2\,g} + O^{2-}{}_{surf}$

Scheme 1. Schematics of the MSR mechanism over Cu-ZnO-Al_2O_3 catalysts.

yield in hydrogen because of lower formation of methane, but also produce more CO.

In Fig. 5 we compare the data obtained at higher temperatures on the catalyst Ni50YSZ calcined at 950 K in conditions (a) (see experimental section) with those obtained in conditions (b) with a catalyst having the composition NiO-ZnO-Al_2O_3 with Ni:Zn:Al atomic ratios of 49.6:21.7:28.7, calcined at 1173 K. These are among the best results in terms of hydrogen yield obtained with these catalysts. In both cases above 750 K the production of hydrogen is limited by the formation of C-containing products other than CO_2, i.e. CO and CH_4. A careful analysis of the products shows that actually in our experimental conditions the equilibrium of WGS is attained above 800 K and the equilibrium of methane SR is attained above 750 K. This means that the hydrogen production is limited by the WGS and methane SR equilibria. The first is likely an unavoidable limit of the ESR process while the other could be avoided only by avoiding methane production.

Thus, an important information concerns the source of methane in our conditions. The reaction has been followed by IR spectroscopy. The data concerning the Ni50-YSZ catalyst are reported in Fig. 6. Ethanol adsorbs in the form of ethoxy groups, characterized by C–O stretching modes at 1103 and 1058 cm^{-1}. These species are at the origin of the formation of both ethylene (by dehydrative decomposition) and acetaldehyde (by dehydrogenation), which are found in the gas phase (Fig. 7) being responsible, respectively, for the typical CH_2 wagging mode at

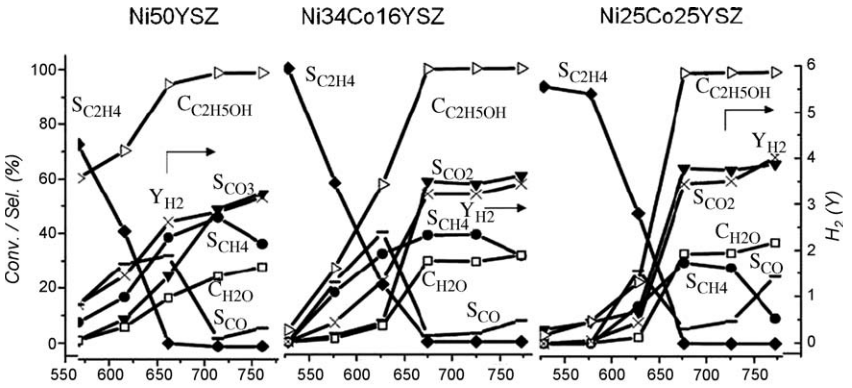

Fig. 4. Conversion of ethanol and selectivities and yields for ESR on Ni(Co)-YSZ catalysts (reaction conditions (a), see experimental section).

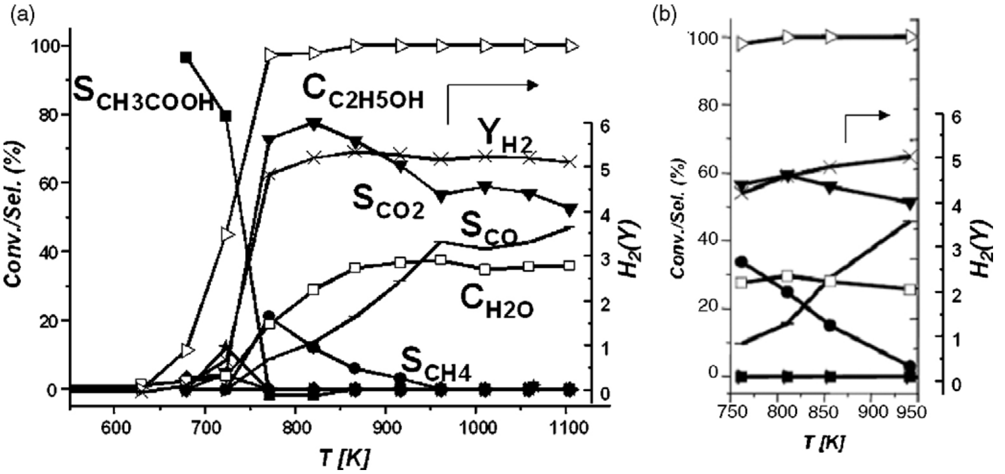

Fig. 5. Conversion of ethanol and selectivities and yields for ESR on Ni-Zn-Al catalyst (reaction conditions (b), see experimental section, left) and on Ni-YSZ catalyst (reaction conditions (a), see experimental section, right).

950 cm^{-1} and for the strong C = O stretching band at 1743 cm^{-1} (masked by the adsorption of gaseous water). Traces of adsorbed acetaldehyde are responsible for a weak CO stretching band at 1695 cm^{-1}, showing that this species easily desorbs. In parallel to the formation of acetaldehyde, surface acetate species also form over this catalyst. At temperatures above 673 K surface formates stoichiometrically decompose into methane and CO (Fig. 7). Thus, we follow by IR the formation of the gas phase species observed as products in the flow reactor. From these data, the mechanism summarized in Scheme 2 accounts for the reaction products we find in our experiments.

To check this mechanism, we performed experiments by varying contact time and water/ethanol ratios on the Ni-ZnO-Al_2O_3 catalysts, where selectivity to the intermediate formaldehyde is higher. The way to SR proposed in the scheme is competitive with dehydration reactions to ethylene and diethylether and this makes quite difficult to provide established conclusions at relatively low temperatures and conversions. In any case, with these catalysts, the concentration to formaldehyde has a maximum at relatively low contact times, while the concentration to acetic acid has also a maximum at higher contact times. This may support our mechanism, although what we suggest is that adsorbed acetaldehyde and vacetate species act as intermediates. This does not necessarily mean that the corresponding gas-phase species also behave as intermediates.

According to our interpretation, also in this case water takes mainly the role of oxidizing the catalyst, which is, in our opinion, a key step also in the WGS and MeSR equilibria. Ethanol/or acetaldehyde is oxidized by the water-oxidized catalyst to acetates. This mechanism is alternative with respect to that occurring via nickel alkyls, nickel carbide, and carbon species, which is supported by several studies in the literature. As reviewed by Røstrup Nielsen et al. [2], these mechanisms are mostly based on Ni single crystal studies performed far from industrial conditions and on DFT calculations also performed on Ni monocrystals [20]. More recent DFT calculations suggest the possibility of formation of oxygenated species on Ni [21]. As we have already remarked, studies of metal monocrystals give likely an incomplete picture of what happens on real supported metal catalysts [22].

According to our interpretation, methane arises from the C2 methyl group of ethanol, which is actually not activated by the catalyst. This means that the production of hydrogen cannot be increased more even if yield is still lower than 4 (i.e. 66%). It is

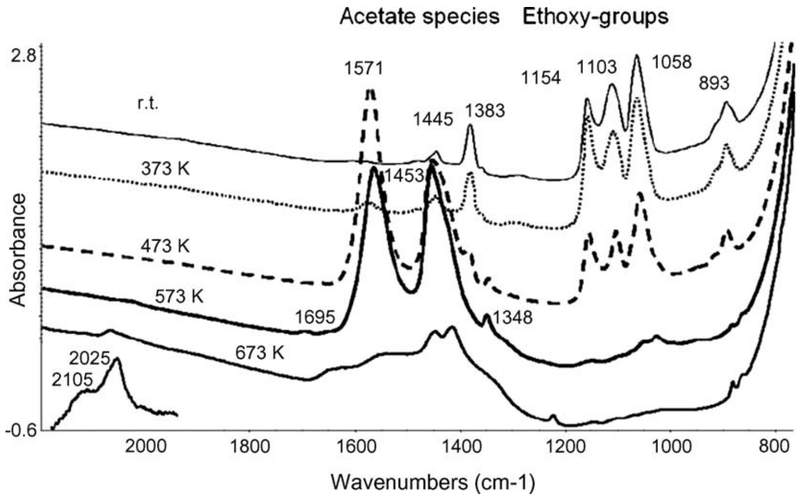

Fig. 6. FT-IR spectra of the surface species upon ethanol adsorption and conversion over Ni (50)/YSZ at increasing temperature.

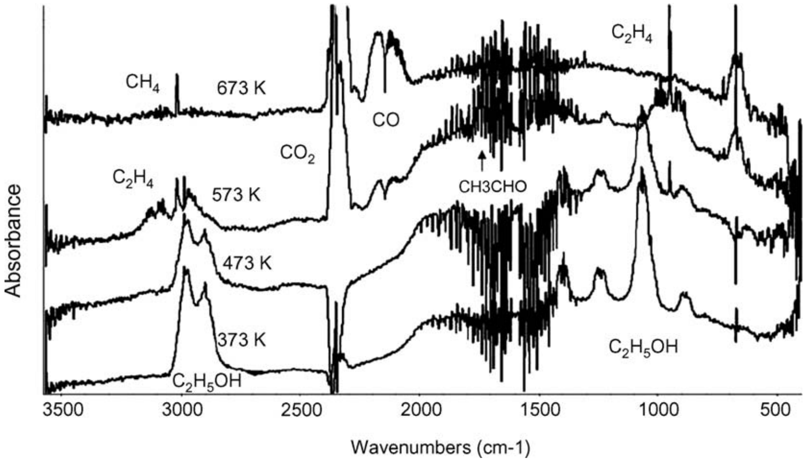

Fig. 7. FT-IR spectra of the gas phase species upon ethanol adsorption and conversion over Ni (50)/YSZ at increasing temperature.

Dissociative adsorption of ethanol / dehydrogenation to acetaldehyde.

$CH_3CH_2OH_g + 2\ O^{2-}{}_{surf} \leftrightarrows CH_3CH_2O^-{}_{surf} + {}^-OH_{surf} \leftrightarrows CH_3CHO_{surf} + H_{2\ g} + O^{2-}{}_{surf}$

Desorption of acetaldehyde

$CH_3CHO_{surf} \leftrightarrows CH_3CHO_g$

Conversion of adsorbed acetaldehyde into acetates

$CH_3CHO_{surf} + 2\ O^{2-}{}_{surf} \rightarrow CH_3\text{-}COO^-{}_{surf} + {}^-OH_{surf} + 2\ e^-$

Decomposition of acetate groups.

$CH_3\text{-}COO^-{}_{surf} + {}^-OH_{surf} + 2\ e^- \rightarrow CH_{4\ g} + CO_g + 2\ O^{2-}{}_{surf}$

Oxidation of methane by the surface (MeSR)

$CH_{4\ g} + O^{2-}{}_{surf} \leftrightarrows CO_g + 2\ H_{2\ g} + 2\ e^-$

Oxidation of CO by the surface (WGS)

$CO_g + O^{2-}{}_{surf} \leftrightarrows CO_{2\ g} + 2\ e^-$

Reoxidation of the surface by water (MeSR and WGS).

$H_2O_g + 2e^- \leftrightarrows H_{2\ g} + O^{2-}{}_{surf}$

Scheme 2. Schematics of the proposed ESR mechanism over Ni-based catalysts.

evident that, if Scheme 2 actually would account for the overall ESR reaction, the hydrogen production would unavoidably be limited

To avoid the formation of methane it is necessary to activate both carbon atoms of methane, or to obtain a deeper decomposition of acetates, which does not seem to be the case for our catalysts.

3.4. *Isopropanol SR over a Pd-Cu/Al_2O_3 catalyst.*

The conversion of the C3 organics propane, propene, isopropanol and acetone in auto-thermal and endothermic SR conditions has been investigated over a Pd-Cu/Al_2O_3 catalyst in a flow reactor [23]. Although several reactions may occur at lower temperatures (like dehydrogenation, oxidative dehydrogenation, dehydration and combustion), SR of 2-propanol, like that of acetone and propane, only start above 850 K and with incomplete selectivity. Cracking and production of methane lower the selectivity to CO*x* and hydrogen. Interestingly, SR of propene starts at significantly lower temperature (600–700 K) than that of isopropanol and is by far the most selective to CO*x* and hydrogen over this catalyst.

4. Conclusions

The reactions of MSR and ESR have been studied over promising catalysts. The MSR reaction over Cu-ZnO-Al_2O_3 catalysts is a very efficient process. Our spectroscopic studied allowed us to propose a mechanism where water takes part of the copper species in a oxidize state and CO is rapidly oxidized to CO2 before leaving the surface. This allows CO production lower than forecast from the WGS equilibrium.

The ESR reaction over Ni-containing catalyst was found to produce organic species like acetaldehyde until 700 K. Above this temperature, the formation of hydrogen is limited by the establishing of the WGS and the MeSR equilibria. Due to the high temperature needed to perform ESR, the WGS equilibrium would likely unavoidably limit the one-step production of hydrogen in this case. It has been concluded that activation of the C2 carbon atom of ethanol of some decomposition product is needed to avoid methane formation and, consequently, the establishing of the MeSR equilibrium. This however is not the case, apparently, of our catalysts.

Preliminary work on isopropanol SR was performed over a Pd-Cu catalyst. Cracking and production of methane lower significantly the selectivity to CO*x* and hydrogen.

Acknowledgements

The authors ackowledge funding from MUR PRIN projects and Dr. Sabrina Presto, Prof. Paola Riani, Prof. Rinaldo Marazza (University of Genova), Dr. Michele Sisani, Prof. Fabio Marmottini (University of Perugia), Dr. M.C. Herrera, Prof. M.A. Larrubia and

Prof. L.J. Alemany (Univ. of Malaga), and Prof. G. Bagnasco and Prof. M. Turco (Univ. of Napoli) for the collaboration.

References

[1] R.M. Navarro, M.A. Pena, J.L.G. Fierro, Chem. Rev. 107 (2007) 3952.
[2] J.R. Røstrup-Nielsen, J. Sehested, J.K. Nørskov, Advan. Catal. 47 (2002) 66.
[3] M. Turco, G. Bagnasco, U. Costantino, F. Marmottini, T. Montanari, G. Ramis, G. Busca, J. Catal. 228 (2004) 56.
[4] D.R. Palo, R.A. Dagle, J.D. Holladay, Chem. Rev. 107 (2007) 3992.
[5] A. Haryanto, S. Fernando, N. Murali, S. Adhikari, Energy Fuels 19 (2005) 2098.
[6] P.D. Vaidya, A.E. Rodrigues, Chem. Eng. J. 117 (2006) 39.
[7] M. Ni, D.Y.C. Leung, M.K.H. Leung, Int. J. Hydrogen Enrgy 32 (2007) 3238.
[8] F. Frusteri, S. Freni, J. Power Sources 173 (2007) 200.
[9] Topsøe hydrogen package plants, www.topsoe.com.
[10] U. Costantino, F. Marmottini, M. Sisani, T. Montanari, G. Ramis, G. Busca, M. Turco, G. Bagnasco, Solid State Ionics 176 (2005) 2917.
[11] G. Busca, U. Costantino, F. Marmottini, T. Montanari, P. Patrono, F. Pinzari, G. Ramis, Appl. Catal. A: Gen. 310 (2006) 70.
[12] G. Busca, A. Vaccari, J. Chem. Soc., Chem. Commun. (1988) 788.
[13] G. Busca, J. Lamotte, J.C. Lavalley, V. Lorenzelli, J. Amer. Chem. Soc. 109 (1987) 5197.
[14] G. Busca, J. Mol. Catal. 43 (1987) 225.
[15] J.M. Gallardo Amores, V. Sanchez Escribano, G. Busca, V. Lorenzelli, J. Mat. Chem. 4 (1994) 965.
[16] V. Sanchez-Escribano, L. Arrighi, P. Riani, R. Marazza, G. Busca, Langmuir 22 (2006) 9214.
[17] M. Turco, G. Bagnasco, U. Costantino, F. Marmottini, T. Montanari, G. Ramis, G. Busca, J. Catal. 228 (2004) 43.
[18] M.A. Larrubia Vargas, G. Busca, U. Costantino, F. Marmottini, T. Montanari, P. Patrono, F. Pinzari, G. Ramis, J. Mol. Catal. A: Chem. 266 (2007) 188.
[19] C. Resini, M.C. Herrera Delgado, S. Presto, L.J. Alemany, P. Riani, R. Marazza, G. Ramis, G. Busca, Int. J. Hydrogen En. 33 (2008) 3728.
[20] R.M. Watwe, H.S. Bengaard, J.R. Rostrup-Nielsen, J.A. Dumesic, J.K. Nørskov, J. Catal. 189 (2000) 16.
[21] C. Pistonesi, A. Juan, B. Irigoyen, N. Amadeo, Appl. Surface Sci. 253 (2007) 4427.
[22] V. Sanchez-Escribano, M.A. Larrubia Vargas, E. Finocchio, G. Busca, Appl. Catal. A: Gen. 316 (2007) 68.
[23] C. Resini, L. Arrighi, M.C. Herrera Delgado, M.A. Larrubia Vargas, L.J. Alemany, P. Riani, S. Berardinelli, R. Marazza, G. Busca, Int. J. Hydrogen En. 31 (2006) 13.