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MOST RECENT RESULTS IN HYDROGEN PRODUCTION FROM GLYCEROL STEAM REFORMING

Here we report the most recent results in hydrogen production through glycerol steam reforming (SR). Glycerol is principally obtained as byproduct of biodiesel production and a glut in its market is expected in the next few years, rendering it an attractive renewable source for hydrogen production. On the contrary of the well known methane and ethanol steam reforming, glycerol SR is not yet so extensively studied and the matter is still quite open. We briefly discuss the general features of the reaction taking into account thermodynamic, mechanism, support role and promotion effects, giving some selected examples on non noble (Ni) and noble metals (Pt, Rh, Ru) based catalytic systems.

Hydrogen is considered to be a good candidate as an alternative energy vector to conventional fossil ones. In particular it is the most promising fuel when used as feed with fuel cells. Up to now hydrogen is almost exclusively produced by reforming of fossil hydrocarbons, especially of natural gas (CH_4>90%) but, due to the more and more restrictive environmental regulations and the consciousness of the depletion of conventional fuels, new production ways are mandatory. Among the different alter-

natives, the H_2 production from biomass is thought to be the most promising. The reforming of alcohols derived from biomass, such as ethanol and glycerol, revealed good chances of application in hydrogen production. Ethanol can be produced by fermentation biomass, such as agricultural products and residues, while glycerol is the main by-product in the biodiesel production by transesterification of oils and fats [1]. Moreover glycerol can be obtained by several other alternative processes, such as hydrogenolysis of sorbitol [2], glucose fermentation [3] and lignocelluloses to ethanol conversion [4]. A huge amount of these alcohols is currently available and their volume of production is going to increase in the next years. In particular glycerol is now considered a promising and economic source of H_2, since its actual market is going to reach a glut due to the increase in biodiesel production [5]. This trend is involving all the global market: for example in Italy biodiesel production is increased from 469.707 t in the 2007 to 694.000 t in 2009 [6] and in the US alone since 2004, biodiesel production has grown from 75 million gallons per year to 650 million gallons per year in 2008 [7]. Transesterification of vegetable oils for biodiesel production yields about 10% wt of glycerol that means the impossibility to adsorb at all its future production in its common applications as cosmetic, medicine and food industry [8]. By-product glycerol typically is a 50%wt mixture of methanol, water, inorganic salts, free fatty acids, unreacted mono-, di- and triglycerides, methyl esters, and a variety of other organic materials in amount dependent to production process. As such, crude glycerol has few direct uses and is of low value and could be addressed as an attractive raw material for hydrogen production.

At present three technologies exist for H_2 production from glycerol: steam reforming (SR), partial oxidation (POX) and aqueous phase reforming (APR). Here we will mainly discuss glycerol SR, for more details on POX and APR technologies we suggest a recent review by Vaidya *et al.* [9].

Reactions involved in glycerol steam reforming are reported in Tab. 1. Reaction (1) represents the overall steam reforming reaction. It is an endothermic transformation, favoured at low pressure, and can be considered as the sum of an endothermic reaction (2), namely glycerol decomposition, and of an exothermic one (4), that is the water gas shift (WGS) reaction. As reported in Tab. 1, many other reactions can take place: CO decomposition to C, CO, CO_2 and C methanation, CH_4 reforming playing the major role. Nevertheless other side reactions, such as dehydration, dehydrogenation, cyclization and polymerization, can lead to coke deposition on the catalysts surface as discussed below (Fig. 1B). Such a complex reaction pathway necessarily requests the design of a robust, reliable and selective catalyst. Moreover a proper choice of reaction conditions becomes a critical point to be addressed.

The general reported mechanism of metal catalysed glycerol steam reforming relates to the one previously proposed for hydrocarbons reforming [11]. Briefly, glycerol SR is an energy intensive process and C-C cleavage is the rate determining step. Glycerol can dehydrogenate and adsorb on metal, subsequent C-C breakings lead to adsorbed CO that can be oxidized through WGS reaction, converted to methane or desorbed. Methane can derive also from CO and CO_2 methanation. Coke can be produced by CO decomposition and the polymerization of the olephines formed during dehydrogenation step. Thermodynamic studies predict that SR is favoured at high temperature, low pressure and high H_2O/C ratio while WGS and methane and hydrocarbon formation are promoted at low temperature. For more detailed thermodynamic aspects we suggest to refer to more exhaustive studies [12-14]. The main problem revealed for the catalytic system during reaction is deactivation that is due to sintering phenomena or fooling. Beside the control of reaction conditions also the tuning of catalytic properties of the materials is useful in order to minimize the deactivation. Up to now many catalytic systems have been investigated, mainly Ni based catalysts but also Pt, Rh, Ru systems supported over different oxides (Al_2O_3, SiO_2, CeO_2, CeO_2-ZrO_2, MgO, Y_2O_3, La_2O_3). Reaction temperature can vary between 350 °C and 900 °C and glycerol amount in the feed varies from 1% to 50% wt. The best catalytic systems are the ones where the synergism between the metal and the support leads to metal stabilization and decreases the rate of coke formation. Supports with low acidity or with basic properties can decrease coking, for examples, the addition of a promoter on alumina such as lanthana resulted in a more stable catalysts [15, 16]. Supports with high oxygen storage capacity, such as CeO_2 and CeO_2-ZrO_2, are also reported to be efficient modifiers in decreasing coke deposition and in promoting WGS reaction [17].

Finally, as a general consideration, a good criticism has to be used when discussing reforming data; in fact, for example, glycerol can undergo thermal pyrolysis before to reach catalysts during evaporation (conversion 65%) to CO, CO_2, H_2, CH_4, olephines (ethylene and propylene) and liquid unsatured compounds (acetone, acetaldehyde, ethanol, propanol, acetic acid, 2,3-dyhydroxypropanal) and almost no direct glycerol reforming happens [18]. Moreover, catalysis conditions can deeply affect results. For example Adhikari [19] reported that at 900 °C glycerol conversion decreased in the order Ni>Ir>Pd>Rh>Pt>Ru for Al_2O_3 monolith supported samples, claiming that the results should be valid only on the given experimental conditions, while in another study on La_2O_3 supported metals, in powder form, the activity order at 600 °C was Ru≈Rh>Ni>Ir>Co>Pt>Pd>Fe [20].

Here we wish to review the catalytic performances in glycerol steam reforming by briefly presenting selected examples of Ni, Pt, Rh, Ru based catalysts (Tab. 2), in particular focusing on catalytic systems and reforming conditions reported in the last five years.

Tab. 1 - Reactions involved in steam reforming of glycerol*	
1 $C_3H_8O_3 + 3H_2O \rightleftarrows 7H_2 + 3CO_2$	+128 kJ/mol
2 $C_3H_8O_3 \rightleftarrows 4H_2 + 3CO$	+250 kJ/mol
3 $C + H_2O \rightleftarrows H_2 + CO$	+131 kJ/mol
4 $CO + H_2O \rightleftarrows H_2 + CO_2$	-41 kJ/mol
5 $C + 2H_2 \rightleftarrows CH_4$	-75 kJ/mol
6 $CO + 3H_2 \rightleftarrows CH_4 + H_2O$	-206 kJ/mol
7 $CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O$	-165 kJ/mol
8 $C + CO_2 \rightleftarrows 2CO$	+172 kJ/mol

adapted from Sutton et al. [10]

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Tab. 2 - List of reviewed catalytic systems

Catalytic systems	T (°C)	Glycerol % wt	References
commercial nickel-based	850	44	21
Ni/Al$_2$O$_3$	600 - 900	47	19
Ni/MgO, Ni/CeO$_2$, Ni/TiO$_2$	550 - 650	47	22, 23
Ni/Al$_2$O$_3$	600 - 700	20	24
Ni/Al$_2$O$_3$	450 - 600	47	25
Ni/Al$_2$O$_3$ modified by Ce, Zr, Mg and La	600	1	26
Ni/CeO$_2$/Al$_2$O$_3$	500 - 600	10	27
Ni/CeO$_2$/Al$_2$O$_3$	700	47	28
Co/CeO$_2$	250 - 550	36	29
Ni-Co/Al$_2$O$_3$	500 - 600	30 - 63	30
Pt/La$_2$O$_3$/Al$_2$O$_3$	500 - 600	10	16
Pt/γ-Al$_2$O$_3$, Pt/ZrO$_2$, Pt/Ce4Zr1α, Pt/SiO$_2$	350	10	32
Pt/Al$_2$O$_3$, Pt/CeO$_2$/Al$_2$O$_3$, Pt/La$_2$O$_3$/Al$_2$O$_3$	250 - 600	30	15
Pt /Al$_2$O$_3$	600 - 900	46	19
Pt/C	350 - 500	36 - 63	33
Pt/Al$_2$O$_3$, Pt/ ZrO$_2$, Pt/CeO$_2$/ZrO$_2$, Pt/MgO/ZrO, Pt/C	225 - 450	30 - 50	34
Rh/Al$_2$O$_3$	450 - 800	36	18
Rh/CeO$_2$/Al$_2$O$_3$	600- 900	46	19
Ru/Y$_2$O$_3$, Ru/ZrO$_2$, Ru/CeO$_2$, Ru/La$_2$O$_3$, Ru/SiO$_2$, Ru/MgO	500 - 600	34	20
Ru/Mg(Al)O	650	10	35
Ir/CeO$_2$	250 - 550	36	29

Ni and non noble metals

In spite of their lower activity and higher tendency to deactivation, with respect to noble metal based catalysts, nickel-based catalysts, and in particular Ni/Al$_2$O$_3$, are commonly used in industry for steam reforming of hydrocarbons because of their low cost and their availability. Ni is active in the C-C, O-H and C-H bonds cleavage and also catalyzes the water gas-shift reaction. For this reason among non-noble metals, Ni could be promising as catalyst also for biomasses steam reforming and has been widely investigated.

Czernik et al. [21] studied steam reforming of biomass-derived liquids, including crude glycerol, employing process conditions similar to those used for steam reforming of natural gases. Promising results were obtained using a commercial nickel-based naphtha reforming catalyst: almost 18 g of H$_2$ was produced from 100 g of "crude glycerol" (76% of the theoretical maximum).

Ni/Al$_2$O$_3$ was found to be the best performing catalyst in terms of H$_2$ selectivity and glycerine conversion among 14 catalysts based on Ni and platinum group metals, supported on Al$_2$O$_3$ or CeO$_2$/Al$_2$O$_3$ monoliths [19]. The reactions were carried out at a flow rate of 0.5 mL/min and at four temperatures from 600 to 900 °C with a molar concentration of glycerol and water 1:6. The maximum conversion with Ni/Al$_2$O$_3$ was reached at 900 °C. The same authors tested the

activity of nickel using MgO, CeO$_2$ and TiO$_2$ as supports [22, 23] studying their catalytic behaviour in different reaction conditions. These supports were selected for the their well known capacities to retard coke formation and to interact with metal promoting catalytic activity.

A more recent work on glycerol steam reforming using nickel-based catalysts was presented by Sanchez et al. [24]. Ni impregnated on alumina was tested under different conditions mainly changing temperature (600-650-700 °C) and weight hourly space velocity (WHSV) (3.4-5.0-10.0 h^{-1}). The results show that higher temperatures and lower WHSVs increase glycerol conversion and the stability of the catalyst (time-on-stream 4 h and 8 h). The increase of WHSV together with the increase of temperature promotes the formation of gaseous by-product as ethane, that could be associated to catalyst deactivation.

The effect of temperature on steam reforming of glycerol using Ni impregnated on alumina was investigated by Buffoni et al. [25]. Catalytic results at temperatures lower than 450 °C showed low conversion to gaseous products, the formation of a plethora of liquid by-products and a fast deactivation of the catalysts. Glycerol conversion to gaseous products is reached at higher temperatures (>450 °C), where C-C cleavage can occur and steam reforming reaction is favoured by thermodynamic.

Although alumina has a good chemical and mechanical resistance, possesses high surface area and can improve metal dispersion, it undergoes to deactivation in the steam reforming of oxygenated compound due to coke formation and sintering of the metallic phase. Coke formation, detected in stability tests, is usually related to dehydration reactions, rearrangement and condensation on the acidic sites of the support. In order to overcome this problem, the support can be modified with other oxidic phases.

A positive effect due to presence of promoters on alumina supported Ni catalyst in the steam reforming of glycerol was shown by Iriondo et al. [26]. The modification of the support with Ce, Zr, Mg and La brings to an improvement in the hydrogen selectivity with respect to the results obtained with classical nickel catalyst supported on bare alumina. The work was based on an in-depth characterization of the catalysts by means of XRD, XPS and TPR analysis and highlights the correlation between modification of the structure and catalytic activity. The different promoters modified in different way the structure of the reference material, depending on the tendency of interaction with support or metal. This changes the surface composition and the metallic surface concentration and properties. Differences in activity were explained in terms of surface nickel concentration in the case of Mg, capacity to activate steam for Zr and stability of metallic phase under reaction conditions when Ce or La were added.

The role and effect of ceria as an alumina modifier in Ni based catalyst in glycerol SR was then studied in details by the same authors

[27]. The promotion with ceria changes the surface properties and the catalytic behaviour of Ni/Al_2O_3 depends on the amount added. At 500 °C low ceria content (4.3 wt% and 8.4 wt%) stabilizes Ni nanoparticles increasing hydrogen yield, maintaining the activity stable during 8 h on stream and reducing the amount of by-products in the liquid phase. Higher ceria contents are not effective for promoting the SR, likely due to the strong interaction of ceria with support that inhibits particles stabilization. Ni supported over bared CeO_2 is not able to convert completely glycerol into products because it suffers a deep deactivation after 2 h on stream at 500 °C.

The effect of noble metal on Ni/CeO_2-Al_2O_3 and the stabilizing role of CeO_2 on active phase were pointed out in another recent work [28].

Recently, Co was proposed as a non noble metal active phase alternative to nickel showing a H_2 selectivity around 90% in the range of 425-550 °C [29] and also the activity of a bimetallic Co-Ni/Al_2O_3 catalyst was evaluated [30].

Noble metals
Pt

Even though in principle Pt can be a good catalyst for glycerol steam reforming due to its ability for C-H activation and C-C cleavage and was extensively studied in APR [31] it is often reported to suffer strong deactivation phenomena ascribable to side reactions promotion. Iriondo tested Pt and Ni catalysts on La_2O_3 modified alumina and found a low activity for Pt catalyst that was ascribed to the high dehydration or dehydrogenation/hydrogenation activity of Pt leading to oxygenated hydrocarbons production. On the other hand, lanthana is reported to modify the acid properties of the support and increase the conversion of oxygenated hydrocarbons to H_2 and CO_2 [16]. The same side products were detected in a study that compares Pt activity on supports with different acidic properties at 400 °C feeding a 10%wt glycerol [32]. A strong deactivation was evidenced for Pt/γ-Al_2O_3 and Pt/ZrO_2 and Pt/α-Al_2O_3(4 wt% CeO_2 - 1 wt% ZrO_2) while Pt/SiO_2 showed complete glycerol conversion up to 40 h. The rate of deactivation followed the acidity

of the support and was related to the formation of side products by dehydration and condensation reactions that were converted into coke during catalysis (Fig. 1B). The reaction was also conducted at 350 °C and at contact times between 0.22 min and 0.88 min in order to evaluate intermediate products. A detailed reaction mechanism was proposed on the basis of the detected products (Fig. 1A). In the first step glycerol undergoes dehydrogenation to 1,3-dihydroxy-2-propanone or to 2,3 dihydroxy-propanal. Starting from 1,3-dihydroxy-2-propanone, through subsequent dehydration, hydrogenation, dehydrogenation, C-C cleavage, hydration steps, acetic acid is formed and finally decomposes to H_2, CH_4, CO and CO_2. Alternatively, 2,3 dihy-
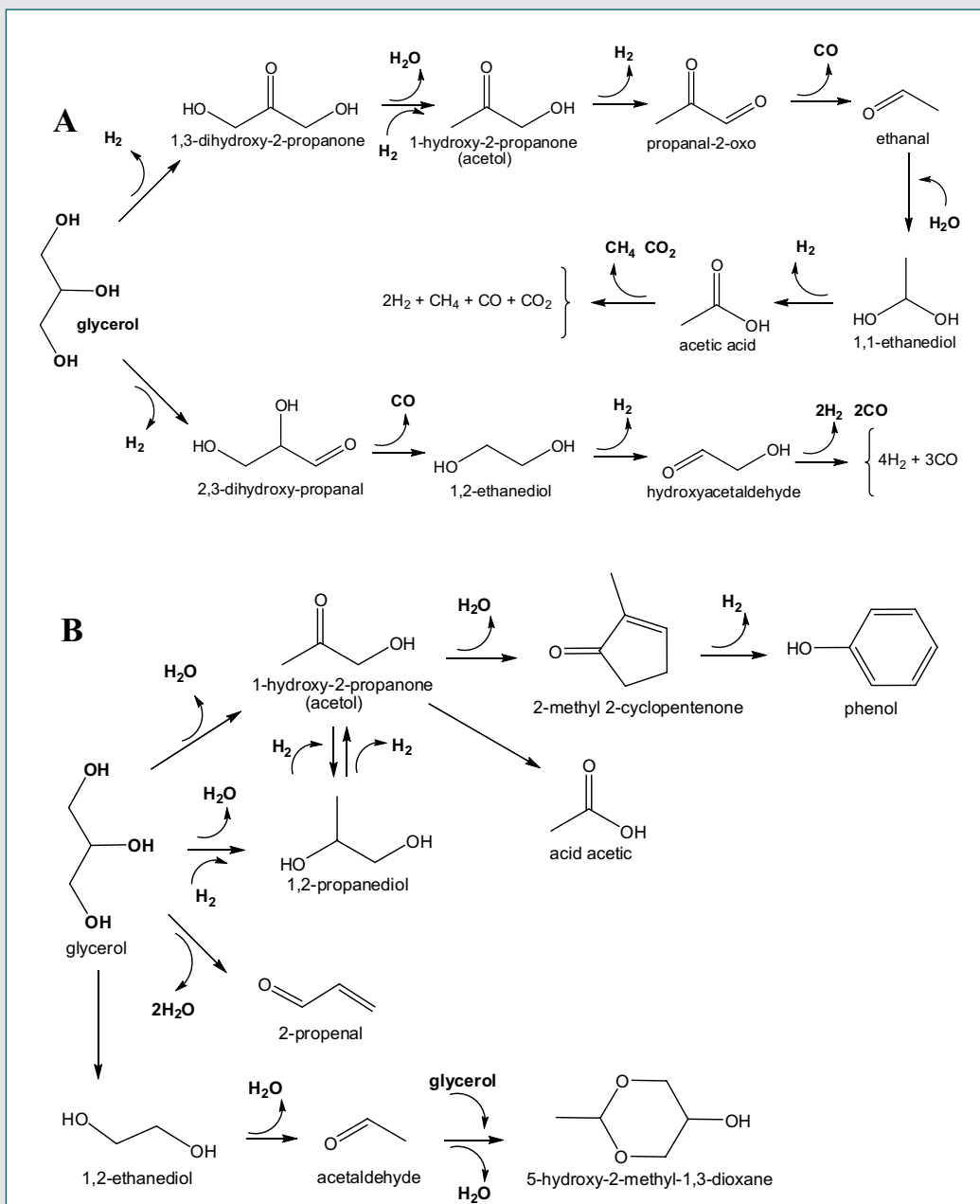

Fig. 1 - A) low temperature glycerol SR mechanism pathway on Pt/Al_2O_3;
B) low temperature mechanism for coke formation on Pt/Al_2O_3 during glycerol SR. Adapted from Pompeo *et al*.

Tab. 3 - Ru based systems performances in glycerol SR					
Catalyst	Conversion	H₂ Yield	Selectivity		
			CO	CH₄	CO₂
Ru(0.5%)/Y₂O₃	100	82.8	20.0	4.4	75.6
Ru(0.5%)/ZrO₂	98.5	81.6	21.7	3.3	74.9
Ru(0.5%)/CeO₂	82.0	73.1	23.6	1.2	75.1
Ru(0.5%)/La₂O₃	87.9	71.8	21.1	4.1	74.9
Ru(0.5%)/SiO₂	32.7	18.3	56.4	3.6	40.1
Ru(0.5%)/MgO	31.1	12.3	72.7	8.7	18.6
Ru(0.5%)/Al₂O₃	28.5	6.4	67.7	13.1	19.2
Ru(0.5%)/Y₂O₃	37.0	26.2	53.1	3.2	43.7
Ru(1%)/Y₂O₃	61.6	49.9	32.2	2.9	64.8
Ru(3%)/Y₂O₃	84.5	65.7	25.8	4.4	69.8
Ru(5%)/Y₂O₃	85.4	65.9	26.5	4.7	68.8

droxy-propanal can be converted into H_2 and CO after dehydrogenation reactions and C-C cleavages. Second reaction pathway was claimed as the main one.

Montini et al. [15] showed that Pt/Al_2O_3 scarce catalytic performances at low temperature were significantly improved by the addition of La_2O_3 and CeO_2 as basic promoters. In the range 350-400 °C Pt/Al_2O_3 had low activity and a significant amount of hydrocarbons was detected. An increase in temperature (>550 °C) promoted CO and H_2 production with small amount CH_4. On the contrary doped systems reached almost complete glycerol conversion to CO and H_2 at 350 °C while CO_2 was produced at higher temperature. Stability test conducted at 350 °C highlighted that CeO_2 doped catalyst rapidly deactivated after 20 h on stream while La_2O_3-doped one maintained stable performances up to 50 h. This was ascribed to a better dispersion of La_2O_3 on the surface of Al_2O_3 that deeper affected support acidity. TGA and HRTEM analysis of samples after catalytic runs allowed to correlate the deactivation to coke formation on Pt surface rather than on NPs sintering.

On Al_2O_3 92% - SiO_2 8% monoliths Pt showed lower performances in comparison with Ni for the SR at high temperatures (600-900 °C) both considering H_2 selectivity and glycerol conversion [19].

Recently, a kinetic study conducted on 5% wt Pt/C at low temperature (T<500 °C) pointed out that glycerol steam reforming is a first order reaction with respect to glycerol when low concentration is used [33]. As the temperature increased from 350 °C to 500 °C the H_2 yield increased from 0.19 to 0.46 mol/mol at a space time equal to 1.56 gh/mol while a decrease of the latter to 0.39 gh/mol caused a yield of 0.31 mol/mol. The gasification of the support was neglected.

Despite the high deactivation of Pt systems reported above, Soares et al. proposed a low temperature glycerol steam reforming to syn-gas process on Pt supported catalysts in order to combine SR with exothermic reactions such as Fischer-Tropsch or methanol synthesis [34]. A strong support influence was revealed: on Al_2O_3, ZrO_2, and MgO/ZrO Pt deactivated during time on stream at 350 °C, only Pt/C

and $Pt/CeO_2/ZrO_2$ performances were stable up to 30 h. Pt/Al_2O_3 maintained stable complete conversion for 25 hours before a sudden drop in activity, while MgO/ZrO activity decreased since the begin. CeO_2/ZrO_2 catalyst had stable performances during all the catalytic test, but lower than that of Pt/C. The mechanism of deactivation was attributed to the formation of C2 hydrocarbons (ethane and ethylene) that was almost negligible for Pt/C. Again deactivation was related to dehydration reactions occurring on the support followed by carbon deposition on Pt surface.

Rh

Rh, as well as Ni, possesses a high activity in C-C cleavage and for this reason it was extensively employed in ethanol steam reforming in the past years. It revealed to be active in glycerol steam reforming too. In fact Rh showed the best performances, both in term of stability and H_2 yield, and lowest coke formation rate on Rh/Al_2O_3 (2.2 mgC/gcat h) compared to Ni catalysts [18]. At 650 °C and 30,000 h⁻¹ the catalysts was stable for 8 h after which H_2 production and conversion drastically decreased due to formation of coke on the metal. TEM analysis revealed the presence of filamentous and of encapsulating coke. Between 650 °C and 700 °C the formation of filamentous coke is prevalent while at 800 °C encapsulating coke caused a strong deactivation of the catalysts.

Doping Rh/Al_2O_3 with CeO_2 seemed to improve performances, showing the system a maximum selectivity to H_2 of 74% at 800 °C and the maximum conversion of glycerol of 87% at 800 °C [19].

Ru

Only few studies on Ru based catalysts for glycerol steam reforming were reported but a systematic studies on Ru supported on Y_2O_3, ZrO_2, CeO_2, La_2O_3, SiO_2, MgO was conducted by Hirai et al. [20]. They revealed that 0.5%wt Ru had the best performances at 600 °C among La_2O_3 supported VIII group metals. Even better activity was shown by Ru on Y_2O_3 with a complete conversion and a H_2 yield of 83%, on the contrary, when Ru was supported on MgO, Al_2O_3 and SiO_2 the conversion of glycerin was very low, around 30%. Moreover, a beneficial effect in conversion and H_2 yield was evidenced when the metal load was increased up to 3% wt at 500 °C (Tab. 3). Conversion and H_2 yield rose from 37% to 85% and from 26% to 66%, respectively, while CO selectivity decreased from 53% to 26%. TGA analysis performed after 6 h and 24 h revealed a weight loss of 0.66% and 0.42%, respectively, demonstrating no deactivation due to coke deposition.

Recently, we revealed a comparable stability for 1% wt Ru supported on Mg(Al)O mixed oxides [35]. At 650 °C a glycerol conversion up to 88% was maintained up to 20 h with a high H_2 yield (>80%), a low CO selectivity (<10%) and no production of CH_4. The CVD synthetic

methodology applied allowed to obtain homogeneously dispersed metal nanoparticles (5 nm) and favoured a strong interaction between the metal and the support as revealed by HRTEM. The addiction of low amounts of Sn on Ru caused no significant changes in conversion while CO_2 selectivity fell down to 51% with CO sel. 44% and CH_4 sel. around 5%. At higher tin loads a deep deactivation and a progressive increase in CO selectivity were evidenced. Tin doping seemed to influence mostly CO and CO_2 selectivity at low Sn/Ru ratio maintaining similar activity, whereas increasing the ratio resulted in a net decrease both of activity and CO_2 selectivity.

Other noble metals were not so extensively investigated in glycerol SR. Among them Ir showed good performances, for examples it was reported that at 400 °C a complete conversion of glycerol was achieved with selectivity to H_2 of 85% over Ir/CeO_2 [29].

Conclusion

Summarizing, in this brief report the catalytic steam reforming of glycerol was reviewed, mainly focusing on the catalytic materials. The reported results clearly show that a full knowledge on glycerol steam reforming process is still missing. A difficulty in rationalizing in a wide context the obtained results was evidenced due to the plethora of reaction conditions that prevents a full comparability among different studies.

In general the analysis of the data underlines the presence of a strong support influence in the reaction performances for all the metals subject of the studies. Anyway Ni can be considered a promising metal taking into account catalytic activity and costs. In particular, beside the commonly used Ni/Al_2O_3, lanthana and ceria doped systems usually show superior performances, in terms of activity and stability. The same effect was also noticed for the noble metals. Pt, despite the good performances in APR, commonly suffers strong deactivation process in SR, while Rh and Ru when compared under the same reaction conditions evidenced better stability.

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RIASSUNTO

Risultati più recenti per la produzione di idrogeno mediante steam reforming del glicerolo

In questo contributo vengono discussi i più recenti risultati che sono stati ottenuti per quel che riguarda lo steam reforming di glicerolo, fonte rinnovabile ottenuta come sottoprodotto del processo di produzione del biodiesel. A differenza di metano ed etanolo, già ampiamente studiati come fonti di idrogeno, nel caso del glicerolo gli studi possono essere considerati ancora non del tutto esaustivi. A tal proposito riportiamo criticamente alcuni esempi selezionati di sistemi basati su metalli non nobili (Ni) e nobili (Pt, Rh, Ru), mettendo in luce brevemente le principali caratteristiche della reazione come meccanismo, termodinamica, effetto del supporto e di promotori.