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On the Support Effect and the Cr Promotion of Co Based Catalysts for the Acetic Acid Steam Reforming

Marta Cortese ^{1,*} , Concetta Ruocco ¹ , Vincenzo Palma ^{1,*} , Pedro J. Megía ² , Alicia Carrero ² and José A. Calles ² 

¹ Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano, Italy; cruocco@unisa.it

² Chemical and Environmental Engineering Group, ESCET, Rey Juan Carlos University, 28933 Móstoles, Spain; pedro.megia@urjc.es (P.J.M.); alicia.carrero@urjc.es (A.C.); joseantonio.calles@urjc.es (J.A.C.)

* Correspondence: mcortese@unisa.it (M.C.); vpalma@unisa.it (V.P.)

Abstract: This work focuses on the support effect of the performances of Co based catalysts for acetic acid steam reforming. SBA-15, a well ordered hexagonal mesoporous silica structure, and CeO₂ have been selected as the supports, with the impact of chromium addition also being investigated. Better acetic acid steam reforming performances have been recorded for CeO₂ compared to SBA-15 supported catalysts and, in particular, the 7Co/CeO₂ catalyst showed the highest values of acetic acid conversions with enhanced H₂ yields below 480 °C, in comparison to the other investigated catalytic formulations. In addition, more pronounced coke depositions and acetone concentrations have been obtained with CeO₂ supported catalysts, due to the tendency of ceria to catalyse the ketonization reaction. Chromium addition to Co/SBA-15 catalysts led to an enhancement in the activity towards acetic acid steam reforming, while on CeO₂ supported catalysts no improvement in the catalysts' activity was observed. However, on both SBA-15 and CeO₂ supported catalysts, Cr addition reduced the amount of coke deposited on the catalysts surface.

Keywords: acetic acid; reforming; hydrogen; cobalt; ceria



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1. Introduction

The increasing levels of CO₂ in the atmosphere, along with the emission of other harmful pollutants (NO_x and SO₂) has led to serious environmental concerns, with experts searching for low-environmental impact sources to solve the current energy crisis. Renewable resources are extremely promising, while the use of biomass as feedstock is encouraged due to its sustainability, wide availability and abundance [1]. Consequently, the use of biomass-derivate compounds (including acetic acid) as a hydrogen source has the potential to reduce the current dependence on fossil fuels [2,3]. Hydrogen is regarded as one of the energetic vectors of the future and its production via reforming of bio-fuels has been widely studied in current literature [4,5]. In 2019, the demand for pure hydrogen was estimated as 70 million tons. The majority of produced hydrogen comes from the conversion of fossil fuels, while only less than 1% hydrogen derives from renewable sources [6]. Among the available feedstocks for hydrogen generation, acetic acid is a promising alternative, with a growing market production expected to reach 18 million tons by 2020 [7].

Acetic acid is mainly produced via methanol carbonylation (~75%) [8]. However, the synthetic route creates severe environmental concerns, due to the release of dangerous by-products and the use of petroleum as feedstock. In addition, this process uses very expensive catalysts. Conversely, extensive research has studied a hydrothermal process [9], which exploits its well-known properties at both high-temperatures and pressures [10]. Other eco-friendly and clean technologies for acetic acid production, including membrane-based processes, are under presently investigation [7].

The conversion of bio-oil obtained via the fast pyrolysis of biomass and its subsequent catalytic steam reforming has been regarded as a feasible and economical route for hydrogen production [11]. Acetic acid is the main component of bio-oil (up to 33%) and its reforming as a bio-oil representative compound has been widely investigated [12]. Bio-based acetic acid steam reforming processes (AcOH-SR) are a potential approach for hydrogen production, which can be directly used in oxide fuel cells or further treated to generate electricity in proton exchange membrane fuel cells [13]. Acetic acid, compared to other biomass-based hydrogen carriers such as ethanol and methanol, is non-flammable and much safer to store and transport [14]. Moreover, the net energy balance for bio-oil production from biomass via integrated fast-pyrolysis is considerably higher than that reported for bioethanol generation (7.01 vs. 1.07) [15].

According to the stoichiometry of the acetic acid steam reforming reaction (Equation (1)), one mole of acetic acid can produce four moles of hydrogen, as a result of the thermal decomposition reaction (Equation (3)) and the water gas shift reaction (Equation (2)). However, the theoretical hydrogen yield is commonly vitiated by undesirable products formation, mainly carbon monoxide, methane and acetone. Methane is mainly formed via decarboxylation (Equation (4)) and acetic acid can also be ketonized to acetone (Equation (5)) [16]. C_3H_6O formation is considered one of the principal causes of coke and high condensation products deposition on the catalyst surface, that leads to catalysts deactivation [17,18]. Moreover, a Boudouard reaction (Equation (6)) and methane decomposition (Equation (7)) are also responsible for coke formation and reduced hydrogen selectivities, contributing to the consequent catalysts deactivation [19,20].

AcOH Steam reforming	$CH_3COOH + 2H_2O \rightleftharpoons 4H_2 + 2CO_2$	$\Delta H = 131.4 \text{ kJ/mol}$	(1)
Water gas shift	$CO + H_2O \rightleftharpoons CO_2 + H_2$	$\Delta H = -41.1 \text{ kJ/mol}$	(2)
Thermal decomposition	$CH_3COOH \rightleftharpoons 2H_2 + 2CO$	$\Delta H = 213.7 \text{ kJ/mol}$	(3)
Decarboxylation	$CH_3COOH \rightleftharpoons CH_4 + CO_2$	$\Delta H = -33.5 \text{ kJ/mol}$	(4)
Ketonization	$2CH_3COOH \rightleftharpoons C_3H_6O + H_2O + CO_2$	$\Delta H = 16.7 \text{ kJ/mol}$	(5)
Boudouard reaction	$2CO \rightleftharpoons C + CO_2$	$\Delta H = -172.4 \text{ kJ/mol}$	(6)
Methane decomposition	$CH_4 \rightleftharpoons C + 2H_2$	$\Delta H = 74.8 \text{ kJ/mol}$	(7)

The design of a proper catalytic formulation is a critical challenge to maximize hydrogen production and limit activity losses [21]. Several active species have been investigated [22–24], showing that hydrogen selectivity decreased in the order $Co > Ni > Rh > Pt$ [25]. According to numerous studies [25,26], cobalt has a reasonable activity for acetic acid reforming at low temperatures, due to its ability to break down both C–C and C–H bonds, along with its competitive price. Moreover, Co displayed very high activity towards water-gas shift reactions at 550 °C. The combination of cobalt with a second metal as a promoter (i.e., nickel or potassium) has shown to improve the coking resistance of the final catalyst, inhibiting, at the same time, the methanation reaction [27,28]. Regarding the choice of the oxide support, alumina is traditionally used for the reforming process, due to its high surface area and mechanical stability. However, the surface acidity promotes acetone and coke precursors formation. Thus, the performance of different supports, capable of enhancing hydrogen yield and deactivation resistance, has been investigated [29]. SBA-15, instead of common amorphous silica, was reported to be a very useful support, capable of preventing Co particles aggregation and metal sintering [30]. SBA-15, a well ordered hexagonal mesoporous (4–12 nm) silica structure presents several attractive characteristics as a catalytic support, such as high specific surface area ($600\text{--}1000 \text{ m}^2 \text{ g}^{-1}$), ease of synthesis, high thermal and mechanical stability [31–33]: the porosity of silica is expected to enlarge the metal-oxide interface with respect to support having lower surface areas, with the purpose to magnify the effect of interaction between metal and oxide. Garcia et al. [34] reported the beneficial effect of Cr addition to Co based catalysts, as a promoter towards hydrogenation–dehydrogenation reactions (i.e., coke precursors hydrogenation). Chromium was also shown to be a textural promoter, reducing the crystallite dimensions and limiting the sintering of the active species [35]; moreover, chromium promoter was

shown to better improve the steam reforming activity of rare earth based catalyst compared to other metals [30,36]. Our previous work [37] highlighted the good performance of a Co-Cr/SBA-15 catalyst in terms of high activity, hydrogen yield and low coke deposition. In addition to SBA-15, other supports, including CeO₂, Al₂O₃, and CeO₂-ZrO₂, have shown promising results for hydrogen production via steam reforming [38,39]. The selection of rare earth oxides allows to exploit the oxygen storage and release capacity of these supports, which are beneficial to preventing and/or removing carbon deposits [40–42]. The reversible redox cycle between Ce⁴⁺ and Ce³⁺ ions generates oxygen vacancies, thus taking or releasing oxygen on the basis of surface requirements and assuring an easy oxidation of carbonaceous species. This property is called as oxygen storage capacity (OSC). An enhancement in coke gasification by steam was reported, along with an improved reforming activity ascribable to the mobile oxygen in the ceria lattice [21]. Thus, ceria not only acts as the support for the active metals but also as an oxygen reservoir. Moreover, the choice of ceria with a high-surface area can reduce the impact of sintering which, together with the boosted contribution of coke gasification, is expected to improve the catalyst activity and stability [43,44]. Furthermore, to the best of our knowledge, Co-Cr/CeO₂ catalysts have yet to be investigated for acetic acid steam reforming. In this study, ceria was therefore chosen as the support to disperse cobalt and chromium.

In this work, a series of Co and Co-Cr catalysts supported on SBA-15 or CeO₂ was prepared, characterized by means of TPR (temperature programmed reduction), XRD (X-ray diffraction method), ICP-AES (inductively coupled plasma atomic emission spectrophotometry), TEM (transmission electron microscope), and SSA (specific surface area) analysis. Subsequently, their catalytic activities were investigated between 400 and 600 °C to study the influence of the adopted support and the chromium effect on the catalyst's performances in terms of acetic acid conversion and hydrogen yield.

2. Results and Discussion

2.1. Catalysts Characterization

The SSA analysis, carried out on the supports and the examined catalytic formulations, are given in Table 1 in which it is possible to note that the SBA-15 samples present higher SSA compared to the CeO₂ based catalysts. Moreover, the chromium addition to 7Co/CeO₂ induces a drastic decrease in the specific surface area of the catalysts compared to the SBA-15 based catalysts. The Cr addition to 7CoCeO₂ lowers the SSA of the 30%, while 2Cr7Co/SBA-15 presents a decrease in the SSA value of only 11%, thus suggesting that the chromium addition on the ceria catalysts may cause a pore filling that lowers the SSA of the catalysts.

Table 1. Results of the specific surface area determination for the analyzed catalysts.

Sample	SSA, m ² g ^{−1}
SBA-15	465
7Co/SBA-15	406
2Cr7Co/SBA-15	362
CeO ₂	105
7Co/CeO ₂	88
2Cr7Co/CeO ₂	62
3Cr12Co/CeO ₂	45

Regarding the H₂ reduction tendency, as reported in current literature, Co supported catalysts are characterized by two main reduction peaks in the range of 300–400 °C, that correspond to the reductions of Co₃O₄ to CoO and CoO to Co⁰, respectively, and an additional broad peak, detected at higher temperatures, resulting from the interactions with the support [45], while crystalline chromia presents a main peak at 250 °C with a shoulder at 180 °C and a weak one at about 360 °C [46].

Figure 1 shows the H_2 consumption trends as function of temperature; not appreciable H_2 consumption was detected for SBA-15, while CeO_2 exhibits a characteristic peak around $480\text{ }^\circ\text{C}$ [47]. Moreover, the presence of the two Co reduction main peaks was encountered for all the analysed samples, whilst the maxima temperature and the intensity of the third peak was strongly affected by the support effect. Comparing 7Co/SBA-15 and 7Co/ CeO_2 , the latter showed a more intense peak at higher temperatures, ascribable to the reduction of Co oxides along with the reduction of the surface shell of Ceria, promoted by the presence of cobalt metal, as reported in current literature [48,49], while the peak showed by 7Co/SBA-15 at higher temperatures may depend on the strong interaction between cobalt oxide particles and the mesoporous support [50,51]. Chromium low temperature reduction peaks have been detected for all the Cr-containing samples, whereas the higher temperature peak resulted overlapped with the cobalt reduction. The Cr addition results in a leftward shift of the cobalt peaks: both 2Cr7Co/SBA-15 and 2Cr7Co/ CeO_2 present lower Co reduction temperatures, indicating lower interaction with the support and/or better active species dispersion [36]. Furthermore, the analysis on the 3Cr12Co/ CeO_2 highlights that an increase in the Cr content causes a shift of the Co peaks to higher temperatures, thus suggesting a mutual interaction between cobalt and chromium species, as described by Chen et al. [52,53].

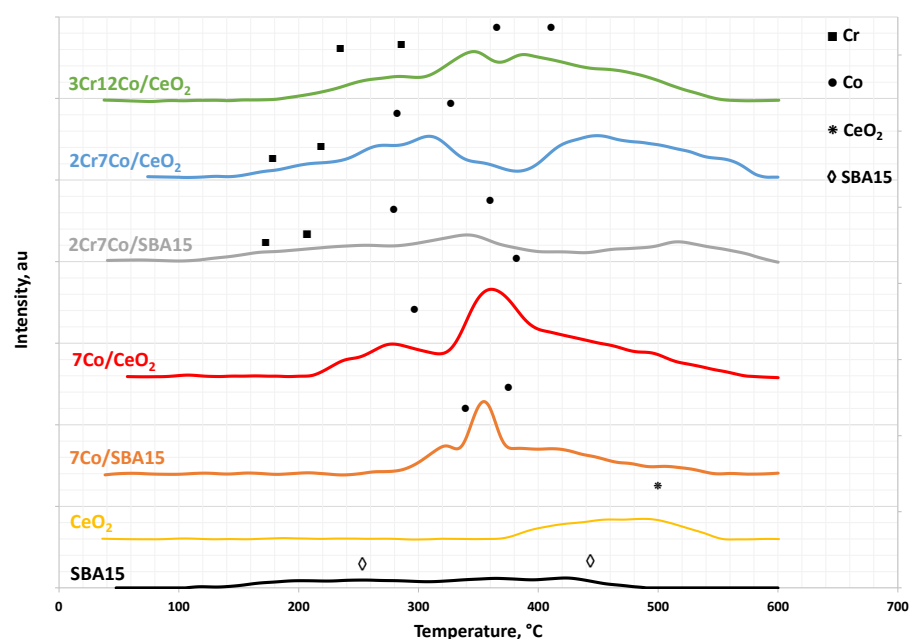


Figure 1. TPR profiles of the tested catalytic formulations and supports.

Figure 2 shows the XRD patterns of the calcined samples. Peaks attributed to cubic Co_3O_4 appear in Co-based catalysts supported over SBA-15 at $2\theta = 31.4^\circ, 37.1^\circ, 45^\circ, 56^\circ, 59.7^\circ, 65.6^\circ, 74.5^\circ$, and 77.8° (JCPDS 01-071-4921) corresponding to the (220), (311), (400), (422), (511), (440), (620), and (533) reflection planes, respectively. Regarding the Co-based catalyst supported over CeO_2 , only peaks with a reflection at $2\theta = 37.1^\circ, 44.9^\circ$, and 65.6° are distinguished, since the diffraction spectra indicated the well-defined and high-intensity major peaks of cubic CeO_2 (JCPDS 01-089-8436), which is constituting the support. These peaks showed the reflection at $2\theta = 28.6^\circ, 33.1^\circ, 47.5^\circ, 56.4^\circ, 59.1^\circ, 69.4^\circ, 76.7^\circ$, and 79.1° . Cr-oxides were not detected in 2Cr7Co/SBA-15, 2Cr7Co/ CeO_2 , and 3Cr12Co/ CeO_2 due to the overlap between the highest diffraction peaks of orthorhombic Cr_2O_3 (JCPDS 00-071-4807) with those of the Co_3O_4 pattern. Furthermore, since the Co content was much higher than the Cr content in all the prepared catalysts, these peaks would have a negligible effect on the XRD patterns, with the Cr species being well-dispersed over the support as reported elsewhere [54,55].

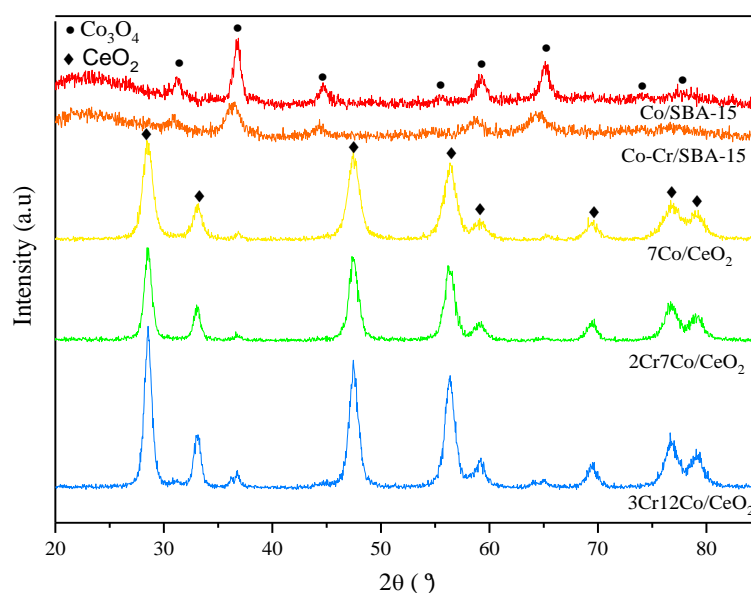


Figure 2. XRD spectra of the investigated catalysts.

Moreover, from the analysis of the crystallite dimensions performed using the Scherrer equation, it is possible to note in Table 2 that the addition of chromium to both the SBA-15 and CeO₂ supported catalysts, remarkably decreased the Co crystallites sizes, thus probably leading to a higher dispersion of the metal species. These results are expected to assure a better AcOH-SR performance.

Table 2. Metal contents in the samples obtained by ICP analysis and diameters of the Co₃O₄ crystallite calculated using the Scherrer equation, from the (311) diffraction plane of Co₃O₄.

Sample	Co Content, wt. %	Cr Content, wt. %	d _{Co₃O₄} , nm
7Co/SBA-15	6.9	-	10
2Cr7Co/SBA-15	6.7	1.8	6
7Co/CeO ₂	5.6	-	18
2Cr7Co/CeO ₂	6.4	1.9	14
3Cr12Co/CeO ₂	9.5	3.0	14

ICP analysis was used to estimate the metals weight percentages in the prepared samples; in Table 2 is possible to observe that, while for the SBA-15 supported catalysts the metal content corresponds to the estimated amounts, the CeO₂ supported samples are characterized by a Co content lower than the predicted values.

In Figure 3 the TEM images of the tested catalysts are shown. As it is possible to notice, CeO₂ and SBA-15 supported catalysts display different structures; indeed, in the SBA-15 supported catalysts, the well-ordered hexagonal mesoporous silica structure is clearly visible from the TEM images (see Figure 3B,D), while for the ceria supported samples the structure of the catalysts appears as agglomerates of spherical particles. Moreover, the dispersion of the active species seems to be higher on the catalysts supported on ceria, thus probably leading to higher performances of the catalysts. In addition, TEM analysis was also performed on the sample 7Co/CeO₂ spent (after the activity test), and as it is possible to see from Figure 3F, the presence of consistent agglomerate of coke was obtained.

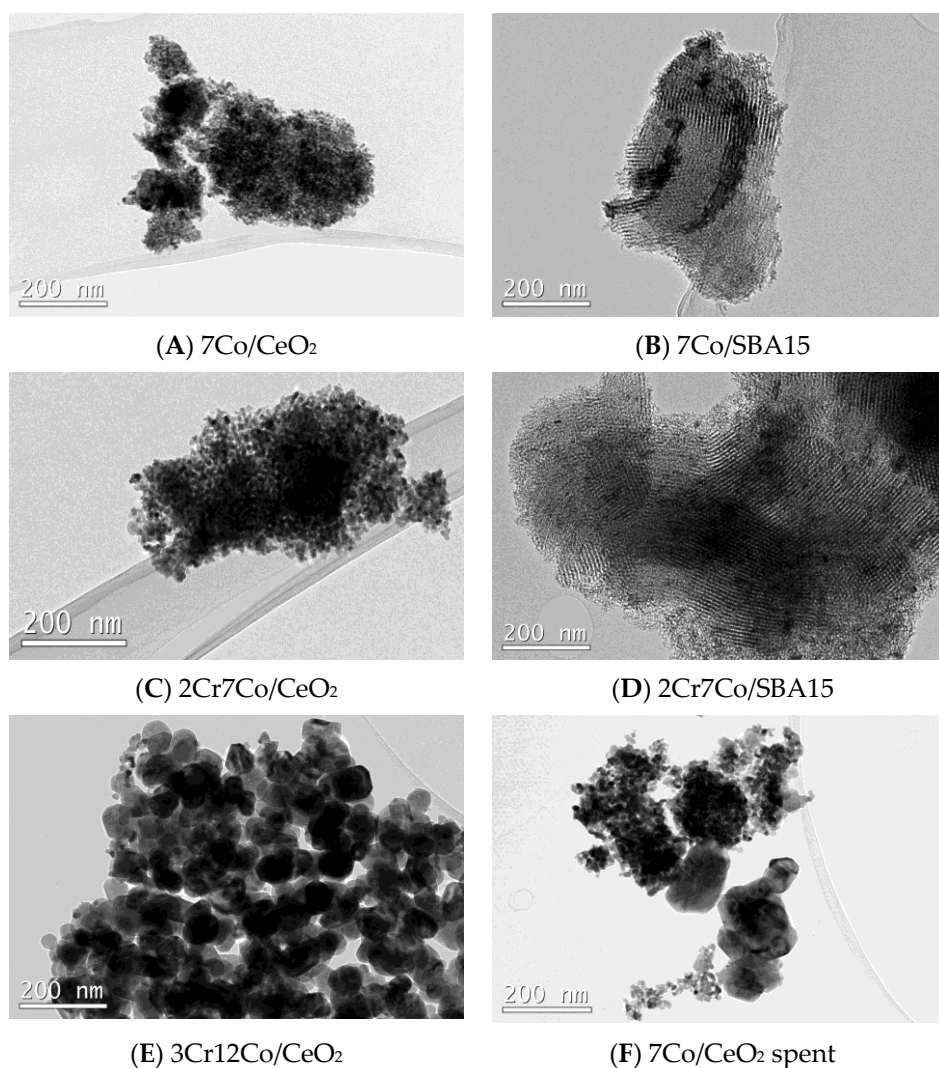


Figure 3. TEM images of the catalysts (A) 7Co/CeO₂; (B) 7Co/SBA15; (C) 2Cr7Co/CeO₂; (D) 2Cr7Co/SBA15; (E) 3Cr12Co/CeO₂; (F) 7Co/CeO₂ spent.

2.2. Activity Tests

2.2.1. Homogeneous Reaction

In order to quantify the contribution of the reaction in the absence of catalysts, a homogeneous reaction test was performed, with the same conditions adopted for the catalytic experiments (AcOH:H₂O:Ar = 1:4:5), but with only quartz flakes within the reactor. Figure 4 shows that a maximum value of 20% was reached for AcOH conversion, descending, however, to zero at 500 °C and giving a low H₂ yield and a considerable C₃H₆O yield. Moreover, analyzing the products distribution presented in Figure 5, one can appreciate the presence in the product streams of CO and CO₂, while methane was not detected, thus suggesting that thermal decomposition and ketonization reactions were taking place, whilst the exothermic decarboxylation was suppressed. Furthermore, no decrease in the water concentration was detected at the reactor outlet (not reported in the graphs), leading to the conclusion that the water gas shift reaction was not occurring.

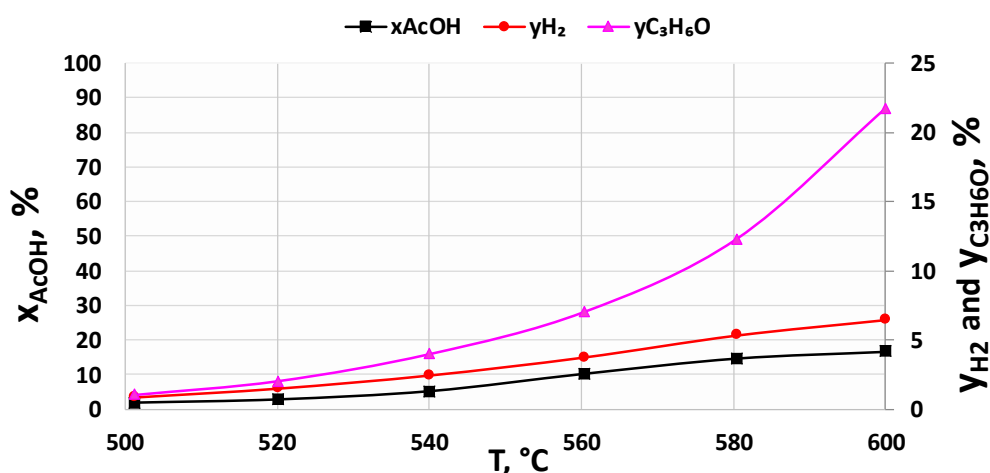


Figure 4. AcOH conversion, H₂ yield, C₃H₆O yield as a function of temperature for the AcOH-SR homogeneous reaction test.

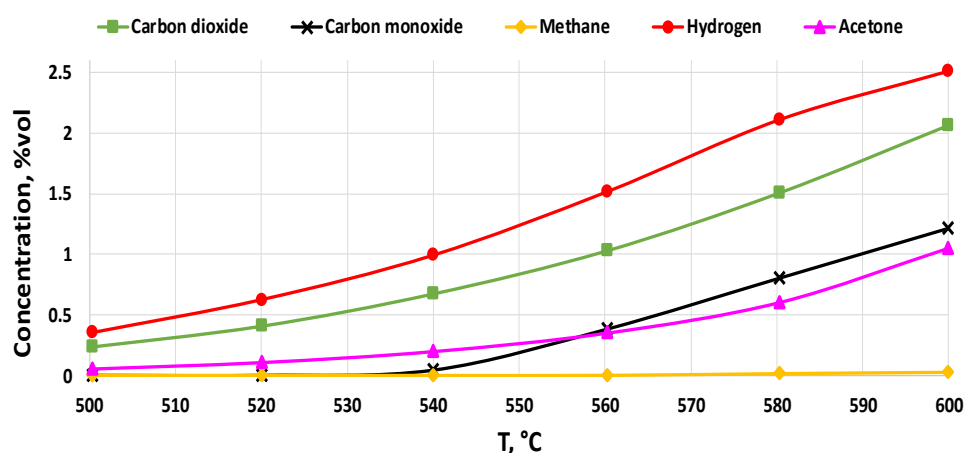


Figure 5. Products distribution as a function of temperature for the AcOH-SR homogeneous reaction test.

2.2.2. Support Effect

Carrying out the AcOH-SR with CeO₂ or SBA-15, without the presence of the active phase, led to different results in terms of AcOH conversion, H₂ yield and C₃H₆O yield, as depicted in Figure 6. The obtained data showed higher acetic acid conversions and H₂ yields on ceria (100% AcOH and ~10% H₂ yield at 600 °C) compared to SBA-15 (23% AcOH and ~2% H₂ yield at 600 °C). However, the conversion dropped to zero at 500 °C, as in the case of the homogeneous reaction. Meanwhile, on SBA-15, around 530 °C the conversion dropped to zero, so the test was stopped before reaching the lowest value of the planned temperature.

In addition, the support choice strongly affected the acetone selectivity of the sample, causing an opposite behavior in terms of acetone formation. While with SBA-15 only a slight concentration of acetone was detected, predominantly at higher temperatures, CeO₂ selection resulted in the promotion of C₃H₆O formation, especially when the temperature decreased; although the ketonization mechanism is still widely debated in current literature, it has been proved the tendency of CeO₂ to convert acetic acid in acetone [56,57]. Moreover, the carbon deposition results, shown in Figure 7 in terms of CFR, show the more pronounced tendency of CeO₂ towards coke formation [17]. Earth metal oxides, compared to silica, are particularly prone to ketones formation, even without the presence of an active metal, due to their acid-base properties [58,59].

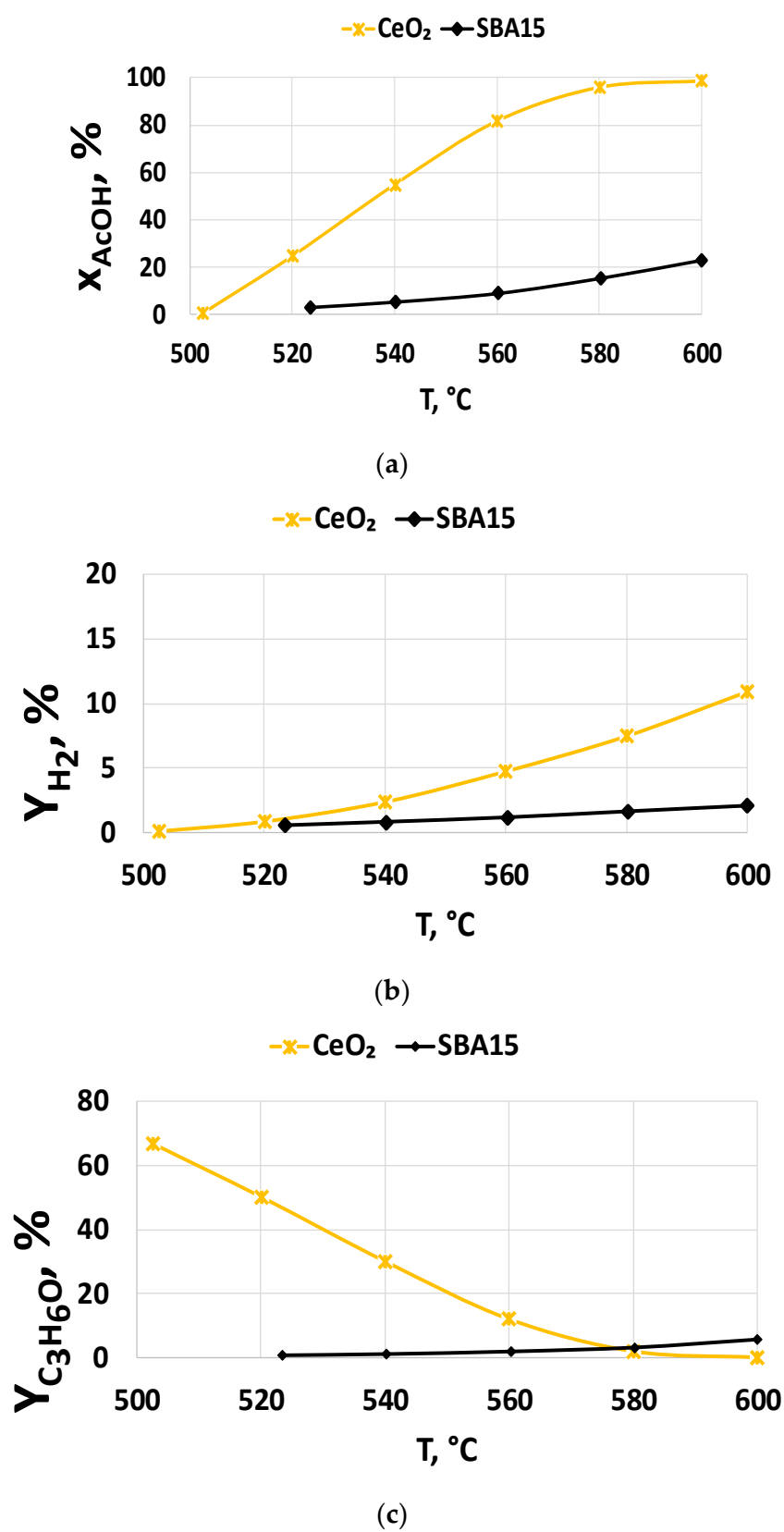


Figure 6. Trends of X_{AcOH} (a), Y_{H_2} (b) and $Y_{C_3H_6O}$ (c) as a function of temperature in the AcOH-SR over CeO₂ and SBA-15.

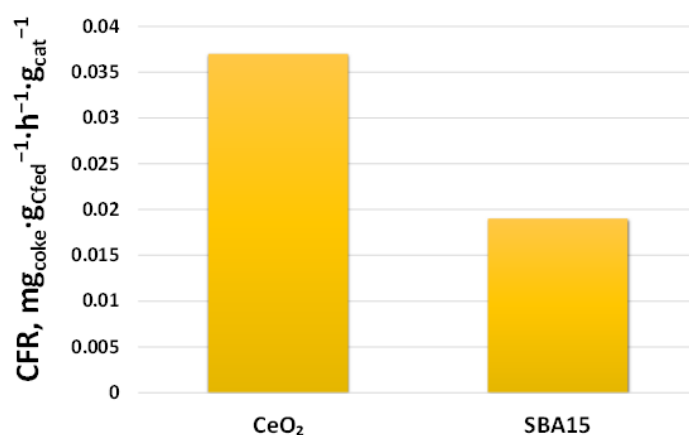


Figure 7. Results of the carbon deposition analysis on the supports.

2.2.3. Catalysts Activity Tests

In Figure 8, a comparison in terms of X_{AcOH} as a function of reaction temperature shows that, between the tested catalytic formulations, the best performances were achieved for 7Co/CeO₂, that exhibited a conversion higher than 90% from 450 °C to 600 °C.

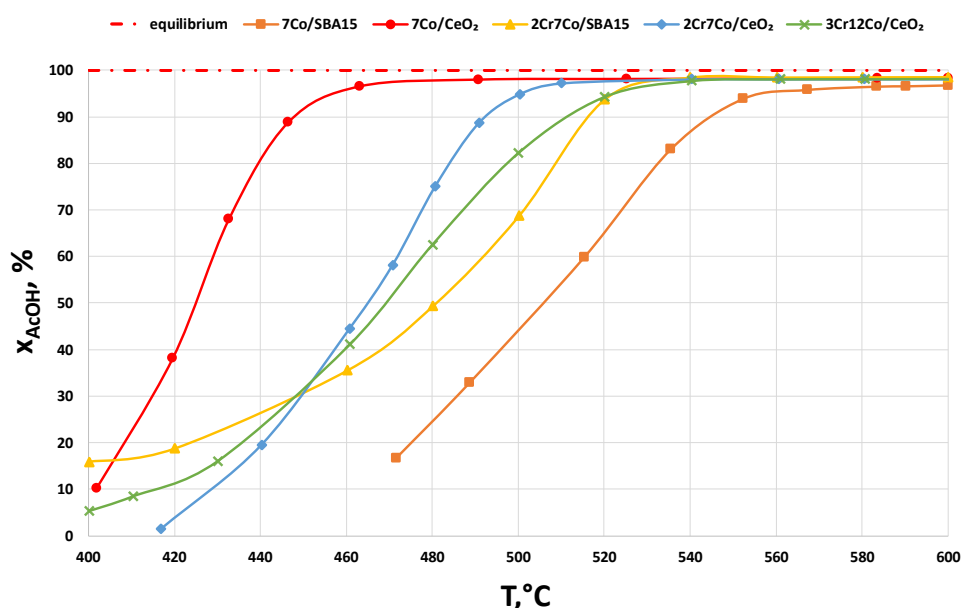


Figure 8. Comparison between the tested catalytic formulations in terms of AcOH conversion as a function of temperature (WHSV = 30h^{-1} , AcOH:H₂O:Ar = 1:4:5).

Compared to the CeO₂ based catalysts, the SBA-15 supported sample displayed, in general, lower AcOH-SR activity. However, the addition of chromium increased the activity of the SBA-15 catalyst, causing a pronounced enhancement of the acetic acid conversion. An opposite behavior was obtained for the CeO₂ supported catalysts; an increase in the Cr content worsened the catalytic performances of the latter samples in terms of AcOH conversion. This result can be explained by looking at the characterization results commented on in Section 3.1 where the elevated decrease of the specific area observed upon Cr addition to 7Co/CeO₂, probably due to a pore filling effect, led to decreased catalyst performances and lower AcOH-SR activity.

Even though the best performances in terms of AcOH conversions were obtained for the catalyst 7Co/CeO₂, higher H₂ yields were gained, as can be seen in Figure 9, above 500 °C, with the addition of chromium; a moderate increase in the H₂ yield was observed

for all the Cr containing samples. This phenomenon, observed for both the CeO_2 and SBA-15 supported catalysts, may be due to the presence of smaller Co particles, obtained after the chromium addition (see Section 2.1), thus resulting in a better Co dispersion. However, below 480 °C, higher H_2 yields are obtained for 7Co/ CeO_2 compared with the other catalytic formulations, thus suggesting that the Cr addition has only a slight effect in increasing AcOH-SR performances over the Co/ CeO_2 catalysts.

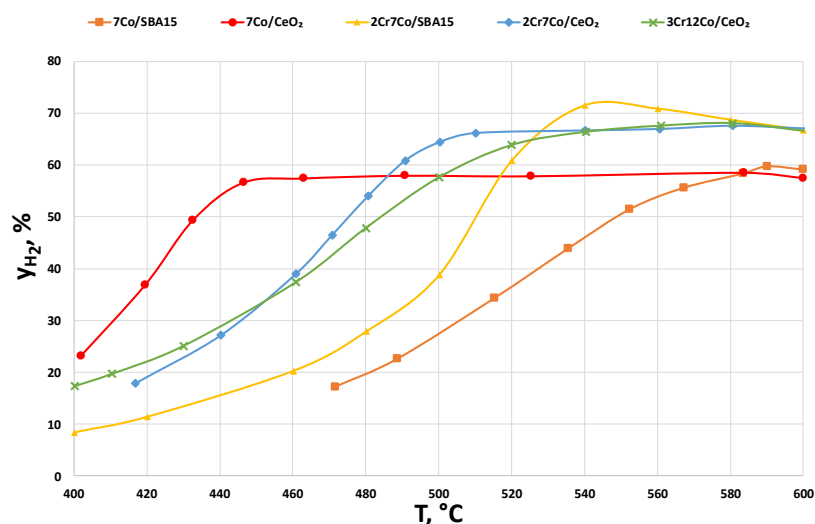


Figure 9. Comparison between the tested catalytic formulations in terms of H_2 yield as a function of temperature.

The results presented in Figure 10, together with the X_{AcOH} trends (see Figure 8), confirmed the strict interconnection between the acetone formation and the catalysts loss in activity. Since acetone was being detected at the reactor outlet, a rapid decrease of the AcOH conversion was observed.

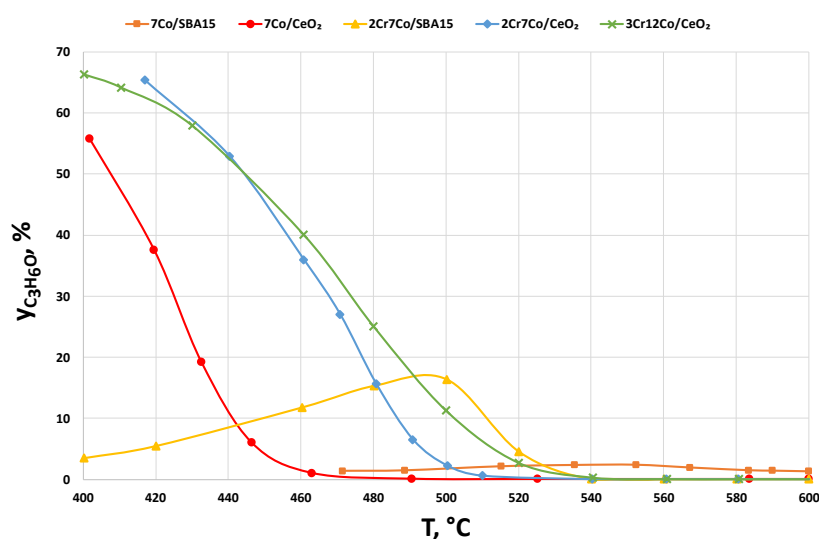


Figure 10. Comparison between the tested catalytic formulations in terms of $\text{C}_3\text{H}_6\text{O}$ yield as a function of temperature.

Moreover, coupling the results relating to the $\text{C}_3\text{H}_6\text{O}$ yields with the carbon deposition analysis, depicted in Figure 11, it is possible to better explain the different coke selectivity of mono- and bi-metallic catalysts. 7Co/SBA-15 showed high values of coke deposits, for which a slight $\text{C}_3\text{H}_6\text{O}$ formation was observed already at high temperatures (~ 600 °C), thus suggesting that the low $\text{C}_3\text{H}_6\text{O}$ concentrations, observed at the reactor outlet, were

ascribable to acetone decomposition and coke deposits formation; a similar phenomenon has already been reported in current literature on a ZrO_2 supported catalyst [18]. The addition of chromium to 7Co/SBA-15 enhanced the catalyst stability, significantly reducing the amount of coke formed ($\sim 0.20 \text{ mg}_{\text{coke}}/(\text{g}_{\text{Cfed}} \cdot \text{h} \cdot \text{g}_{\text{cat}})$ for 2Cr7Co/SBA-15 compared to $\sim 0.29 \text{ mg}_{\text{coke}}/(\text{g}_{\text{Cfed}} \cdot \text{h} \cdot \text{g}_{\text{cat}})$ for 7Co/SBA-15). Although at $\sim 520^\circ\text{C}$ acetone was detected at the reactor outlet and the AcOH conversion dropped to low values, at lower temperatures ($\sim 480^\circ\text{C}$) $\text{C}_3\text{H}_6\text{O}$ yields decreased, leading to a reduced amount of deposited coke for 2Cr7Co/SBA-15 compared to 7Co/SBA-15; this aspect can be seen in Figure 10, in which the peak present in the acetone yield trend clearly suggests that, below 480°C , the acetone concentration is lowered, maybe due to the presence of acetone reforming reactions or due to the inhibition of the ketonization reaction. A similar behaviour was observed for the CeO_2 supported catalysts upon chromium deposition. The interconnection between acetone appearance and the catalysts loss in activity was also encountered on the CeO_2 catalysts.

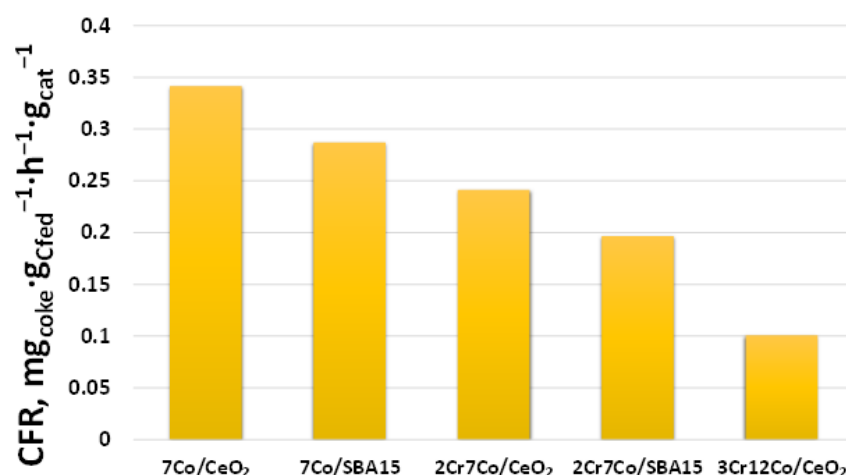


Figure 11. Results of the carbon deposition analysis carried out after each activity test on the spent catalysts.

The 7Co/ CeO_2 catalyst exhibited no acetone traces and conversions $>90\%$ above 460°C , while for 2Cr7Co/ CeO_2 and 3Cr12Co/ CeO_2 the conversion dropped, and the acetone formation was already observed at higher temperature values ($\sim 500^\circ\text{C}$). Moreover, the sample 3Cr12Co/ CeO_2 showed, at low temperatures (below 420°C), a decrease in the slope of the acetone formation, thus highlighting the advantage obtained with the Cr addition in terms of coke formation. Carbon deposition decreases according to the order: $7\text{Co}/\text{CeO}_2 > 2\text{Cr}7\text{Co}/\text{CeO}_2 > 3\text{Cr}12\text{Co}/\text{CeO}_2$, highlighting the advantage obtained with the Cr addition in terms of coke formation: an increase in the chromium content leads to lower carbon depositions. However, contrary to what was observed for the SBA-15 supported catalysts, between the CeO_2 based samples, the catalyst that exhibited the highest value of deposited coke was also characterized by higher AcOH conversion values (see Figure 8). This result can be ascribed to the improved activity of CeO_2 based catalysts towards both acetic acid reforming and ketonization reaction, as already discussed for the bare supports.

3. Materials and Methods

3.1. Preparation and Characterization of the Catalysts

Co and Co/Cr catalysts, supported over mesostructured SBA-15 material, were prepared through the incipient wetness impregnation and co-precipitation method using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as precursor salts (purchased by Sigma-Aldrich, St. Louis, MO, USA), as described elsewhere [30]. The SBA-15, used as the support, was syn-

thetized according the hydrothermal method described for the first time by Zhao [31]. On the other hand, mono and bi-metallic CeO₂ supported catalysts were prepared through a wet impregnation and co-precipitation method using Co(NO₃)₂·6H₂O and Cr(NO₃)₃·9H₂O as precursor salts. Commercial CeO₂ (ACTALYS[®] HSA 5 purchased by Solvay, Spinetta Marengo AL, Italy) was adopted as a support. It was first calcined at 600 °C for 3 h and subsequently impregnated in a solution of the Co and Cr salts precursors at 120 °C until complete water evaporation. Afterwards, the obtained powder catalysts were dried and calcined at 600 °C for 3 h.

Table 3 presents a list of the catalytic formulations prepared in this work.

Table 3. Summary of the synthesized catalysts.

Sample	Support	Co Content, wt. %	Cr Content, wt. %
7Co/SBA-15	SBA-15	7	-
2Cr7Co/SBA-15	SBA-15	7	2
7Co/CeO ₂	CeO ₂	7	-
2Cr7Co/CeO ₂	CeO ₂	7	2
3Cr12Co/CeO ₂	CeO ₂	12	3

The prepared catalysts were characterized by means of TPR analysis, SSA determination, XRD and ICP-AES.

Samples reducibility was evaluated through TPR analysis, carried out in-situ under a reducing stream (5% H₂/Ar) and heating up the reactor from room temperature to 600 °C with a 5 °C/min heating rate.

TEM micrographs were obtained through a Philips TECNAI 20 microscope (200 kV) with a resolution of 0.28 nm.

The SSA analysis was realized in a Costech International Sorptometer 1040 Kelvin. The samples were degassed at 105 °C for 30 min and then, the SSA evaluation performed by N₂ dynamic adsorption at −196 °C. Then, the SSA determination was obtained through the B.E.T. equation.

The Co and Cr contents in the prepared catalysts were determined using ICP-AES in a Varian VISTA-PRO AX CCD-Simultaneous ICP-AES spectrophotometer. The samples were previously treated by acidic digestion using H₂SO₄ and HF.

All the X-ray diffraction measurements were collected at room temperature by means of a Philips X'pert PRO diffractometer using Cu Kα radiation and, subsequently, the Scherrer equation was used to calculate the mean crystallite sizes.

3.2. Experimental Activity

All the experimental tests were conducted using a tubular fixed-bed reactor (AISI 316L stainless steel 37 cm, o.d. 13 mm, i.d. 9 mm), in which the catalyst was fixed between quartz wools; the reactor was placed vertically in a heated furnace and the gas temperature was measured in correspondence to the end section of the catalytic bed by means of a K-type thermocouple.

The H₂O/AcOH liquid mixture, stored in a tank under nitrogen pressure and fed by a mass flow controller for liquids, was firstly mixed with argon, and then sent to a stainless-steel boiler at 260 °C, in order to reach a complete vaporization and good mixing of the total reactor inlet flow rate. Furthermore, the boiler outlet mixture, by means of two 4-way valves, could be alternatively sent to either the reactor or the purge, reaction or bypass configurations, through $\frac{1}{4}$ " stainless steel pipes, heated at 160 °C, to avoid any possible condensations. In the bypass configuration, nitrogen could be used as the inert gas in the operations of heating up or cooling down.

The reactor outlet products stream was continuously analysed by means of a Hiden Analytical mass spectrometer, observing 2, 16, 18, 28, 40, 43, 44, and 58 fragments in order to evaluate the concentration of H₂, CH₄, H₂O, CO, Ar, AcOH, CO₂, and C₃H₆O, respectively. A scheme of the experimental set up in the tests is presented in Figure 12.

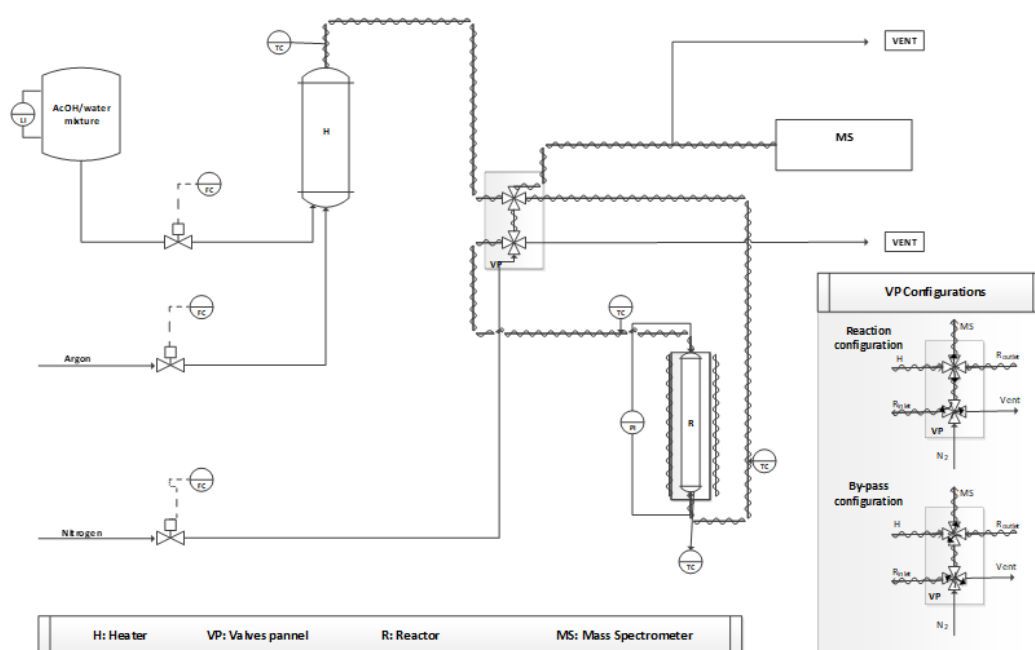


Figure 12. Scheme of the experimental set up.

All the prepared catalytic formulations were tested under the same experimental conditions, with a WHSV (weight hourly space velocity) of 30 h^{-1} , defined as the ratio between the total mass flow rate fed to the reactor and the amount of catalyst loaded into the reactor. The feeding mixture was composed of volumetric percentages of 10% AcOH, 40% H_2O and 50% Ar, characterized by a $\text{H}_2\text{O}/\text{AcOH}$ molar ratio equal to 4. Furthermore, as the different tested catalysts presented various density values, in order to have comparable fluid dynamic conditions in all the tests, 1 g of powder catalyst ($180\text{--}355 \mu\text{m}$) was diluted with different amounts of $500 \div 710 \mu\text{m}$ quartz flakes to keep constant a total bed volume of 2.5 cm^3 .

Prior to the evaluation of the catalytic performances, the carbon, hydrogen and oxygen balances closure were checked to ensure the validity of the experimental results, with an error lower than 5% being considered acceptable.

Furthermore, the catalytic performances were evaluated in terms of AcOH conversion (X_{AcOH}), H_2 yield (Y_{H_2}) and $\text{C}_3\text{H}_6\text{O}$ yield ($Y_{\text{C}_3\text{H}_6\text{O}}$) with the below formulas, where n represents the number of moles.

$$X_{\text{AcOH}} = \frac{n_{\text{AcOH},\text{in}} - n_{\text{AcOH},\text{out}}}{n_{\text{AcOH},\text{in}}} \cdot 100\% \quad (8)$$

$$Y_{\text{H}_2} = \frac{n_{\text{H}_2}}{4 \cdot n_{\text{AcOH},\text{in}}} \quad (9)$$

$$Y_{\text{C}_3\text{H}_6\text{O}} = \frac{2 \cdot n_{\text{C}_3\text{H}_6\text{O}}}{n_{\text{AcOH},\text{in}}} \quad (10)$$

The experimental procedure was as follows: prior to any catalytic test, the samples were reduced as reported in Section 3.1. Subsequently, the catalysts activity was evaluated in the temperature range of $600\text{--}400 \text{ }^\circ\text{C}$ in a descending order, with a cooling rate of $2 \text{ }^\circ\text{C}/\text{min}$.

After each run, the carbon deposition was evaluated in terms of carbon formation rate (CFR), defined as follows (Equation (11)):

$$\text{CFR} = \frac{m_{\text{C}_{\text{coke}}}}{g_{\text{Carbon,fed}} \cdot h \cdot g_{\text{catalyst}}} \quad (11)$$

In which: m_{coke} [g] indicates the total amount of coke deposited during the test, $g_{\text{Carbon, fed}}$ [g] represents the whole quantity of carbon fed during the reaction experiments, h [h] the time elapsed and g_{catalyst} [g] the weight of catalyst loaded in the reactor.

The carbon formation rate expression has been already reported for reforming reactions [60]. The amount of carbon deposits on the catalysts surface was estimated by exposing the spent catalyst to air and heating up to 600 °C (2 °C/min) and evaluating the consequent difference in weight.

4. Conclusions

In this work, a series of Co and Co-Cr catalysts supported on SBA-15 or CeO₂ was prepared, characterized by means of TPR, XRD, ICP, and SSA analysis, and subsequently tested in the ACOH-SR in order to study the influence of the adopted support and the chromium addition effect on the catalytic performances.

Carrying out the AcOH-SR on the bare supports (SBA-15 and CeO₂) highlighted their different products selectivities: CeO₂ use, compared to SBA-15, led to obtain higher acetic acid conversions and H₂ yields, but also higher C₃H₆O concentrations and coke deposits, due to the tendency of CeO₂ to catalyse the ketonization reaction.

The activity tests, performed on the different catalytic formulations, showed that the Cr addition to Co-based catalysts had different results depending on the support used. A chromium addition to Co/SBA-15 catalysts led to an enhancement in the AcOH-SR performances, thus resulting in an enhancement of the AcOH conversion, while on CeO₂ supported catalysts, there was no improvement. This behaviour could be explained as follows. The addition of Cr to Co/CeO₂ supported catalysts resulted in reduced Co particles dimensions on the catalysts surface, as in the case of SBA-15 supported catalysts, but the higher SSA decrease, probably due to a pore filling effect. The increase of the chromium content in the catalysts causes a worsening in AcOH conversion and H₂ yields while the only obtained advantages are gained in terms of coke deposition. In order to better exploit the CeO₂ properties, an advantageous opportunity could be the use of more basic promoters, capable of inhibiting ketonization reactions.

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