Catalytic Oxidation of Vinyl Chloride over SrCO₃-Co₃O₄ Catalysts: Effect of the Sr:Co Molar Ratio

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Co_3O_4 catalysts modified with $SrCO_3$ with various Sr:Co molar ratios were synthesized by a co-precipitation method and their catalytic behavior was examined for the gas-phase oxidation of vinyl chloride. The physical-chemical properties of the samples were thoroughly characterized by means of ICP-AES, BET measurements, XRD, H_2-TPR, XPS and SEM-EDX. The obtained results revealed that the incorporation of strontium carbonate introduced changes in the textural and structural properties as well as modifications in the surface chemical composition of the catalysts. The performance of the samples was found to be controlled by the concentration of active species on the surface (Co^{2+}/Co^{3+} and O_{ads}/O_{latt} ratios) and the reducibility of the samples. As for the stability of the catalysts, clear evidences of deactivation (more severe when increasing the $SrCO_3$ content) were noticed, probably caused by the decomposition of the $SrCO_3$ phase and the formation of $SrCl_2$ accompanied by a loss of textural properties and active surface oxygen species.

1. Introduction

Chlorinated volatile organic compounds (Cl-VOCs) are a large group of compounds characterized by low molecular weight, low boiling point and the presence of at least one chlorine atom in their structure. Their release to the atmosphere is mainly due to industrial activities. Most of them are employed as intermediates in textile dyeing and printing industries, pharmaceutical industries, electronic equipment manufacturing and fine chemicals industries, among others (He et al., 2019). These organochlorinated compounds are responsible for the formation of photochemical smog, depletion of ozone-layer and harmful effects on human health, among others, which together with their stability and inertness make them persistent organic pollutants (Li et al., 2020a). In view of the magnitude of the problem, governments and public administrations are pushing for the development of technologies that effectively reduce emissions of these pollutants in industrial effluents with minimal economic impact. Among the treatment methods for the control and removal of Cl-VOCs, catalytic oxidation is the preferred strategy considering its high efficiency in the treatment of highly diluted off-gases with low energy consumption and no secondary pollution (Liu et al., 2021a). The selection of a suitable catalyst is the principal operational parameter of this technique. The most used catalysts for this purpose can be classified into three main groups: noble metal catalysts, mixed-metal catalysts and non-noble metal oxide catalysts. Noble metal catalysts perform an outstanding activity in oxidation reactions however they are very expensive and sensitive to chlorine poisoning (Li et al., 2020b). Mixed-metal catalysts (Fe-Ce, Mn-Ce, Co-Ce, or Ce-Ti) are complex oxides which contain two or more transition metal oxides. The addition of a second metal cation can improve some properties of the catalyst such as its reducibility, a property of particular relevance in VOC oxidation reactions (Kamal et al., 2016). Finally, non-noble metal oxides have been shown to be more resistant to chlorine poisoning than noble metals and their cost is much lower, making them a very interesting alternative to noble metals catalysts. Along with others, cobalt-based catalysts have been employed in a wide range of catalytic processes including the oxidation of Cl-VOCs with superior catalytic performance. The catalytic activity of cobalt oxide is related to the crystal phases, oxidation states, oxygen vacancies and reduction ability (weak Co-O bond strength), and mobile oxygen species inside its lattice (Chen et al., 2022). All these physical-chemical

properties are closely related to the preparation method. Therefore, strategies following optimized synthesis routes that enhance these properties and/or doping with other metals, generally lead to improved catalytic behavior. Interestingly, Feng et al., (2018) found that doping a Co/CeO_2 with strontium promoted the reducibility, enlarged the specific surface area, and introduced defects and oxygen vacancies which may improve the catalytic performance of the catalyst in the total oxidation of toluene.

Thus, the target of this work focuses on examining cobalt oxide catalysts modified with strontium carbonate synthesized through an optimized preparation method based on the Kirkendall effect aimed at obtaining hollow nanotubes, for the oxidative gas phase removal of trace amounts of vinyl chloride (VC), selected as a model chlorinated compound due to its recalcitrant character and wide industrial application.

2. Experimental

Four catalysts with varying Sr:Co molar ratio (0.1, 0.2, 0.3 and 0.4) have been prepared following a co-precipitation method based on the Kirkendall effect. In a typical procedure, two ethanolic solutions of cobalt acetate tetrahydrate and strontium acetate hemihydrate (Alfa Aesar) with adjusted concentrations were mixed with an ethanolic urea solution (VWR Chemicals). The temperature was maintained at 65 ºC under stirring. First, the solution was dark purple, then it turned paler and finally a pink precipitate was thoroughly formed. After an ageing stage of 4 h at constant temperature (65 ºC), the precipitate was collected by filtration, washed with ethanol and dried at 80 ºC overnight. Finally, the precursor was calcined under controlled atmosphere (5% O_2/He) at 250 ºC, cooled down to room temperature and recalcined at 500 ºC during 3 h. The heating ramps were 0.5 and 1 ºC min^{-1} for each calcination step, respectively. The as-synthesized catalysts were denoted as SrCox, where x is the Sr:Co molar ratio.

The physical-chemical properties of the synthesized samples were evaluated by means of several characterization techniques, namely ICP-AES, XRD, BET, SEM-EDX, XPS and temperature-programmed techniques. The catalytic tests were carried out in a tubular fixed-bed reactor with 0.85 g of catalyst and a feed of 1,000 ppm of VC at a flow rate of 500 cm^3 min^{-1}, obtaining a gas hourly space velocity of 15,000 h^{-1}. The catalytic efficiency was explored in the temperature range 150-500 ºC. The feed and effluent streams were analyzed by gas chromatography, volumetry and potentiometry.

3. Results and discussion

3.1. Physical-chemical characterization

Prior to characterization, the samples were pelletized to obtain a particle size between 0.08-0.16 mm.

The structural properties of the catalysts were evaluated by X-ray diffraction between 5 and 80º at 2θ. The instrument used was an automatic diffractometer model X'Pert PRO from PANaltical using Cu Kα radiation and a Ni filter. The obtained patterns (Figure 1a) confirmed the coexistence of the two oxide phases (Co_3O_4 and $SrCO_3$). Thus, the diffraction peaks located at 2θ=19.2º, 31.3º, 36.9º, 44.8º, 59.4º and 65.2º were characteristic of the cubic Co_3O_4 spinel structure (ICDD 01-078-1969), while those at 2θ=25.2º, 25.8º, 29.6º, 36.6º, 41.5º, 44.1º, 47.7º and 50.2º corresponded to the $SrCO_3$ phase (ICDD 01-084-1778), which verified that the $SrCO_3$-Co_3O_4 composite catalysts were successfully synthesized. Moreover, no other diffraction peaks related to CoO or other impurities (precursor remnants) were detected. On the other hand, it could be observed that the ratio between the peaks at 2θ=36.9º (Co_3O_4) and 25.2º ($SrCO_3$) decreased as the Sr:Co molar ratio increased, which confirmed a raise of $SrCO_3$ content in the samples. This Sr enrichment was verified by ICP-AES analysis. The measurements were performed in a Horiba Yobin Yvon Activa instrument where the samples were previously dissolved in aqua regia. As shown in Table 1, the experimental values were very similar to the nominal ones, except for the SrCo0.3 catalyst, which was somewhat higher.

The textural properties of the samples were evaluated by N_2 physisorption with a Micromeritics TRISTAR II 3020 instrument. Prior to the analysis the samples were degassed at 200 ºC for 10 h with N_2 flow. The main results are summarized in Table 1. All samples exhibited type IV isotherms with H1 hysteresis loops, indicating that the mesoporous structure was preserved after the strontium addition. Moreover, it could be noticed that as the content of $SrCO_3$ increased, so did the surface area of the catalysts from 19 to 26-32 m^2 g^{-1}. This observation could be provoked by the introduction of Sr into Co_3O_4 lattice, which could limit the growth of cobalt nanocrystals in accordance with XRD results (9-12 nm for SrCox oxides compared with 22 nm for the pristine Co_3O_4 sample). A similar finding was reported by Feng et al., (2018) when doping CeO_2 with Sr.

Table 1. Physical-chemical properties and activity data in the catalytic oxidation of VC over the SrCO₃-Co₃O₄ composite catalysts.

| Catalyst | Sr:Co ratio (ICP-AES) | S_{BET}, m^2 g^{-1} | V_{pore}, cm^3 g^{-1} | d_{pore}, Å | $D_{Co_3O_4}$, nm | H_2 consumption, mmol g^{-1} | XPS | | 1st cycle | | 2nd cycle | |
							Co^{2+}/Co^{3+}	O_{ads}/O_{latt}	T_{50}, ºC	T_{90}, ºC	T_{50}, ºC	T_{90}, ºC
Co_3O_4	-	19	0.05	200	22	16.6	0.64	0.63	255	285	265	305
SrCo0.1	0.12	21	0.06	140	10	13.1	0.59	0.65	260	350	300	355
SrCo0.2	0.24	19	0.05	140	10	11.3	0.85	1.25	220	245	295	330
SrCo0.3	0.38	26	0.07	150	12	9.5	0.78	1.02	230	275	315	375
SrCo0.4	0.44	32	0.08	140	9	8.2	0.89	1.25	225	250	315	350

* After performing 3 catalytic tests on each sample the standard deviation has been set at ± 4ºC at low T (conversion < 50%) and ± 2ºC at high T (conversion > 50%).
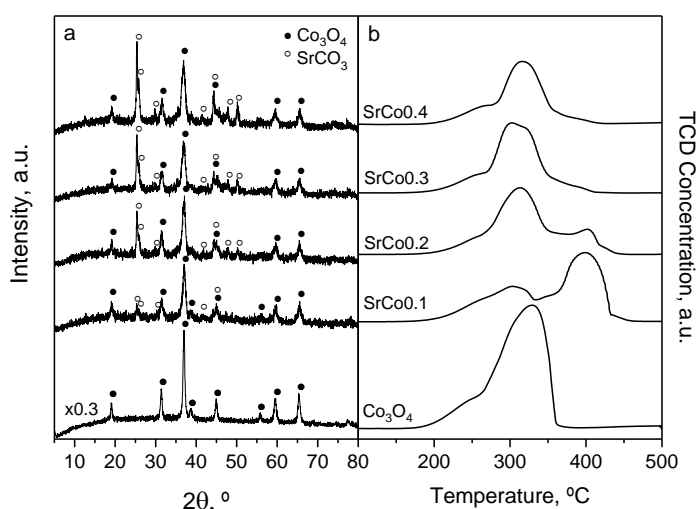

Figure 1. XRD diffractograms and H_2-TPR profiles of the SrCO₃-Co₃O₄ composite catalysts.

The redox behavior of catalysts in oxidation reactions is closely related to their catalytic performance. Furthermore, it is widely accepted that unsaturated C=C bonds, as in the case of vinyl chloride, are difficult to dissociate and oxidize over catalysts with poor reducibility (Dai et al., 2019). The redox properties of the prepared catalysts were evaluated by temperature-programmed reduction with hydrogen (H_2-TPR) from room temperature to 500 ºC on a Micromeritics Autochem 2920 instrument equipped with a TCD detector. It is known that Co_3O_4 typically follows a two-step reduction process; first, Co^{3+} species present in the mixed oxide are reduced to Co^{2+} followed by the reduction of these to metallic cobalt (González-Prior et al., 2018). The corresponding reduction profiles of the SrCox samples, along with the profile of pure Co_3O_4 oxide, are compared in Figure 1b. Notable differences in the shape of the reduction profiles were evident as a function of the Sr content. While in the case of the blank Co_3O_4 catalyst, two more or less discernible peaks associated with the sequential reduction of Co^{3+} to Co^{2+} and Co^{2+} to Co^0 were observed at 260 and 330 ºC, respectively, the sample with a Sr:Co=0.1 molar ratio exhibited two major reduction peaks at 305 and 400 ºC with two shoulders at 260 and 350 ºC. As the SrCO₃ content of the samples increased, this second peak at 400 ºC was less visible and disappeared for Sr:Co molar ratios higher than 0.3. These results suggest that the addition of large quantities of Sr favored the reduction of cobalt oxide by decreasing the temperature of the reduction peaks with a shift of about 15 ºC. Conversely, the incorporation of trace amounts of Sr worsened the overall reduction of the samples, possibly due to a strong chemical interaction between Sr and Co_3O_4 that strengthened the Co-O bonds, making it difficult to split them and consequently the reduction of Co_3O_4 (Li et al., 2018). The hydrogen consumption of each sample is shown in Table 1. As expected, it decreased as the Sr:Co molar ratio increased and in all cases it virtually coincided with that theoretically expected for the actual Co_3O_4 content of each sample, as determined by ICP-AES.

The surface composition and chemical state of the composite catalysts were evaluated by means of XPS analysis in view of the key role played by surface Co^{2+} and O_{ads} species in oxidation reactions (Zhang et al., 2021). These measurements were performed on a Kratos AXIS Supra spectrometer using a 120 W Al Kα monochromatic radiation source with a pass energy of 160 eV for the general survey and 20 eV for the specific spectra. The $Co2p_{3/2}$ XPS profile (Figure 2a) could be deconvoluted into five peaks. Co^{3+} species in octahedral sites were represented by the peak at 779.0 eV, meanwhile the peak at 780.1 eV was ascribed to surface Co^{2+} species in tetrahedral sites. The other three contributions at 781.5, 784.8 and 789.3 eV were attributed to CoO species and shake-up satellites of CoO and Co_3O_4, respectively. On the other hand, the O1s spectra could be decomposed into four peaks corresponding to several types of surface oxygen species with different chemical states (Figure 2b). The bands at 529.3 and 530.8 eV were correlated to lattice and adsorbed oxygen species, whereas the peaks at 531.7 and 533.1 eV were attributed with the presence of adsorbed carbonates and water. It should be noted that the contribution of the signal at 531.7 eV was increasingly larger as the $SrCO_3$ content in the samples increased, in coherence with a favored presence of Sr as evidenced by the Sr3d spectra (not shown). Table 1 summarizes the Co^{2+}/Co^{3+} and O_{ads}/O_{latt} molar ratios, estimated by integrating the areas of the XPS peaks, for the composite catalysts. A direct relationship between the concentration of Co^{2+} and the population of adsorbed oxygen species (O_{ads}) could be established, which in turn is related to the generation of oxygen defects. Therefore, a higher value in the Co^{2+}/Co^{3+} ratio with respect to the theoretical value of 0.5 could result in a higher catalytic activity.

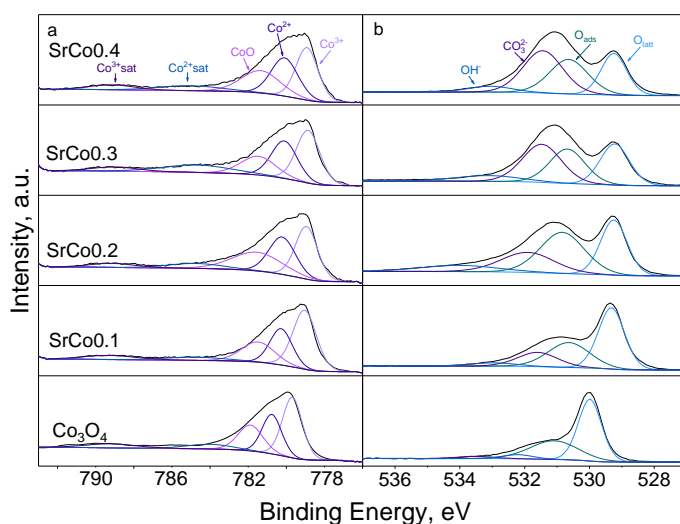*Figure 2. XPS profiles of the $SrCO_3$-Co_3O_4 composite catalysts.*

3.2. Catalytic behavior of the $SrCO_3$-Co_3O_4 composite catalysts

The catalytic performance of the samples was evaluated by means of the light-off curves between 150 and 500 ºC which are presented in Figure 3. Moreover, the corresponding values of T_{50} and T_{90} are summarized in Table 1. The bare Co_3O_4 catalyst resulted highly active in the catalytic oxidation of VC, with T_{50} and T_{90} values of 255 and 285 ºC, since the thermal decomposition in the absence of any catalyst was lower than 50% at 550 °C. After the incorporation of strontium carbonate, the catalytic efficiency of the samples was appreciably boosted in the following order: SrCo0.2 > SrCo0.4 > SrCo0.3 > SrCo0.1. This decrease in T_{50} values was in fairly good agreement with the Co^{2+}/Co^{3+} and O_{ads}/O_{latt} molar ratios evidenced by XPS (Figure 4). Thus, the catalyst with a molar ratio Sr:Co=0.1 showed a better catalytic behavior than the bare Co_3O_4 catalyst in the temperature range 150-250 ºC. However, above 250 ºC a flattening of the conversion curve occurred, which may be due to catalyst deactivation caused by the adsorption of Cl species produced during VC decomposition. Similarly, for SrCo0.2 and SrCo0.3 catalysts, catalytic activity suffered a decrease (more severe when the molar ratio Sr:Co was 0.3) in the temperature ranges 300-325 ºC and 300-375 ºC, respectively (Liu et al., 2021b).

Together with a notable activity, high selectivity is desirable in chlorinated VOCs oxidation reactions, that is, avoiding the generation of by-products sometimes more harmful than the initial pollutant. In VC oxidation over the pristine Co_3O_4 catalyst the main detected by-products were tetrachloromethane, trichloromethane, cis-1,2-dichloroethylene and to a lesser extent dichloromethane and trans-1,2-dichloroethylene. After the incorporation

of SrCO$_3$, the formation of chlorinated by-products was considerably reduced. This could be due to the preference of Cl for Sr atoms, which protected cobalt from chlorination and resulted in a lower chlorinated by-products generation (Lin et al., 2021). In fact, among the SrCO$_3$-modified samples the SrCo0.1 catalyst produced the highest amount of by-products.
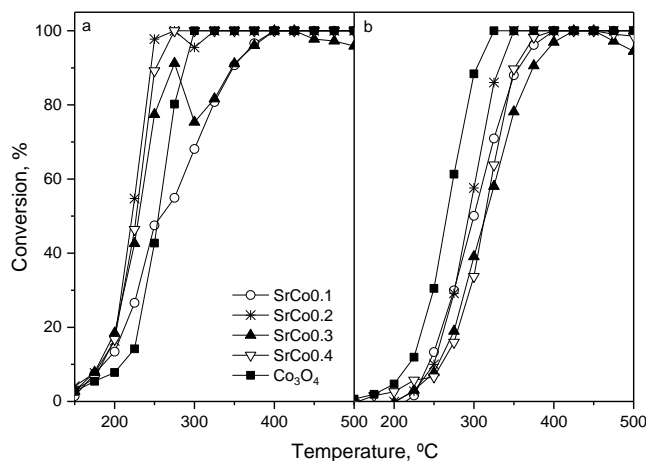

Figure 3. Light-off curves of the oxidation of VC over the SrCO$_3$-Co$_3$O$_4$ composite catalysts: a) 1st cycle, b) 2nd cycle.
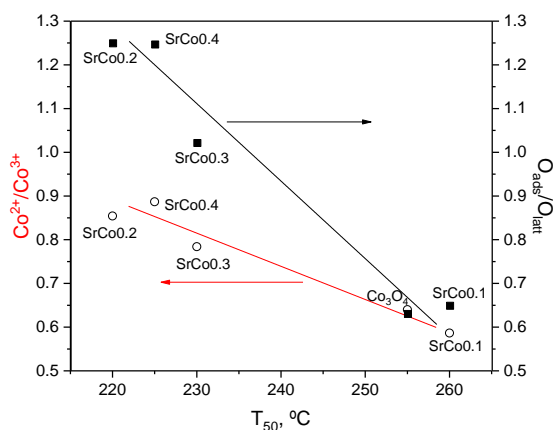

Figure 4. Relationship among Co^{2+}/Co^{3+}, O$_{ads}$/O$_{latt}$ molar ratios and T$_{50}$ values.

In view of the behavior exhibited by the catalysts during a second reaction cycle, all the oxides modified with strontium carbonate showed signs of deactivation (T$_{50}$ values increased between 40 and 90 ºC), which became more severe as the Sr content of the sample increased. The post-reaction samples were characterized by X-ray diffraction. It was observed that the SrCO$_3$ was transformed into SrCl$_2$ after two consecutive reaction cycles. This surface chlorination was as well confirmed by XPS and SEM-EDX. SEM-EDX analyses were obtained on a JEOL JSM-6400 scanning electron microscope coupled to an INCA EDX detector at 20 kV, 1nA and 10 mm. The results revealed a chlorine content in the samples between 6-18 wt.%, close to the expected for a stoichiometric strontium chloride phase. Along with this phase transformation, the crystallite size also enlarged, and the surface area dramatically decreased. Thus, it could be deduced that catalysts deactivation could be due to surface chlorination coupled with a loss of textural properties. Globally, the results derived from this study concluded that although Sr addition was highly efficient for potentially promoting the oxidation ability of Co$_3$O$_4$, the simultaneously enhanced affinity for chlorine species limit the use of these Sr-Co composites for chlorinated VOCs oxidation.

4. Conclusions

A series of SrCO₃-Co₃O₄ catalysts with different Sr:Co molar ratios were prepared following a co-precipitation route. The synthesized samples were thoroughly characterized (N₂ physisorption, ICP-AES, XRD, SEM-EDX, H₂-TPR and XPS) and evaluated for the complete oxidation of vinyl chloride. It has been found that the incorporation of SrCO₃ improved textural and structural properties of the catalysts owing to the introduction of Sr into Co₃O₄ lattice restraining its crystallization. Moreover, the introduction of strontium led to changes in the composition of the Co₃O₄ surface, generating more Co²⁺ and O₍ads₎ species, highly desirable in oxidation reactions. In fact, the activity data seemed to be governed by the population of active surface species. On the other hand, the promoted redox ability also played a determining role in VC oxidation. SrCo0.1 sample exhibited poor redox properties which resulted in the formation of many incomplete oxidation by-products leading to catalyst deactivation. As for the stability of the samples, clear evidences of deactivation (more severe when increasing the Sr content) were observed in consecutive reaction cycles. An exhaustive characterization of the post-reaction samples confirmed the decomposition of the SrCO₃ phase and the formation of SrCl₂ (inactive) associated with a loss of textural properties and active surface oxygen species.

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