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Performances of Co-based catalysts for the selective side chain oxidation of toluene in the gas phase

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Dedicated to Prof. Ferruccio Trifirò for his 65th birthday and his continuous effort in stimulating innovation and understanding in heterogeneous catalysis.

Abstract

The performances of some cobalt-based catalysts (mixed oxides derived from Co–Al hydrotalcite precursors, cobalt supported on alumina and SBA-15, and a Co–Mn perovskite) in the selective oxidation of toluene to benzaldehyde are analyzed by temperature-programmed reactivity tests. Only one sample ($CoO_x/CoAl_2O_3$ mixed oxide derived from a hydrotalcite precursor and having a Co:Al ratio of 2) was found active and selective and further examined in flow reactor transient reactivity tests. The latter tests confirmed the results, but indicated a fast deactivation. The analysis of the catalytic performances of this sample in the presence or absence of oxygen and the results of temperature-programmed desorption tests after toluene and oxygen absorption suggest that a different reaction mechanism from the more known Mars–van Krevelen redox mechanism (oxidation by lattice oxygen and reoxidation of the reduced catalyst) could be responsible for the catalytic performances of these catalysts. A series of evidences indicates that tentatively adsorbed oxygen, possibly as peroxo species, are present on the catalysts and responsible for the catalytic behavior. It is also shown that the presence of CO_2 in the feed reduces the rate of deactivation, possibly due to the formation of more stable peroxocarbonate species.

Keywords: Co-based catalysts; Side chain oxidation; Toluene; $CoO_x/CoAl_2O_3$

1. Introduction

The commercial processes of selective side chain oxidation of alkylaromatics are mainly based on homogeneous catalysis (Co-acetate with Mn and Br salts as activators) in solvents such as acetic acid and using oxygen as oxidant [1–4]. The use of this solvent is required for two principal reasons: (i) low flammability and (ii) possibility of good recovery of the products (acids) by crystallization. The typical reaction temperatures are about 160–180 °C and therefore the synthesis requires the use of autoclave reactors which, however, should be made using special and costly materials due to the corrosive medium. In addition, when aldehydes instead of acids are the target products and/or substituents (which enhance the solubility) are present on the aromatic ring, the yields obtained during product recovery (by crystallization) are low. Furthermore, the formation of brominated byproducts (using bromine as activator) is an issue. Therefore, incentives in terms of process simplification and lower environmental impact exist for the development of a new heterogeneous catalytic process for the synthesis of (substituted) aromatic aldehydes.

Various patents have been reported on the synthesis of substituted benzaldehydes, usually based on vanadium as the key component [5–11], although various additional components are present in the complex formulations. Vanadium has been also often the key component in catalysts reported in the literature, applied especially for studying the model reaction of toluene selective oxidation to benzaldehyde [12–21].

Molybdenum-based catalysts show also an interesting behavior. Yoo et al. [22] reported that zeolites onto which Fe and Mo were introduced by chemical vapour deposition (CVD) show excellent properties in *p*-xylene selective

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oxidation. Iron-molybdates are well-known catalysts for the oxidation of methanol to formaldehyde [23], but are not extensively applied in other selective oxidation reactions, because they completely oxidize several substrates [24]. They become selective when a limited oxygen concentration is present in the feed, e.g. when the limited availability of surface oxygen could provide site isolation around the adsorbed intermediate and avoid overoxidation to carbon oxides. However, catalyst productivity and stability are poor. The reducibility of iron-molybdate may be instead controlled by forming nanoparticles inside a rigid (zeolite) matrix [25]. A good promotion of the performances in aromatic aldehyde formation from the corresponding alkyl aromatic (especially halo-substituted aromatics) has been reported [25], but the limit is the low rate of back-diffusion of the products of reaction out from the zeolitic cage [26]. An alternative possibility is the site isolation of molybdenum sites by adding cerium to the binary Fe–Mo-oxide system [5,27].

In all cases, there are various results indicating that the reaction mechanism of these solid catalysts is based on the classical allylic H abstraction and nucleophilic oxygen insertion mechanism. Trifirò et al. [28] were the first who recognized the role of metal–O bond (in particular, double bond) in the mechanism of selective oxidation, and several further experiments have proof and extended the concept [29]. Instead, in homogeneous phase a radical-like mechanism promoted by the redox Co^{3+}/Co^{2+} cycle occurs [3,4]. In the process of oxygen incorporation into the oxide structure, various types of electrophilic (radical-type) activated oxygen species form before being incorporated as a structural (''lattice'') oxygen of the oxide. It was extensively discussed in the past that these adsorbed-oxygen (charged and/or radical-type) species are responsible of the non-selective oxidation of hydrocarbons [30,31], although in some cases they may have a selective behavior especially in alkane activation [1,32] and references therein. However, no evidences have been reported, as far as we know, about a possible role of adsorbed-oxygen species in the gas-phase selective oxidation of alkylaromatics to the corresponding aldehydes.

Due to the differences in the reaction mechanism, no attempts have been made to consider Co as a possible active element also for the heterogeneous gas-phase oxidation of alkylaromatics. Co-molybdates (in particular ternary compounds with other elements such as Ni or Fe) are known catalysts for the oxidative dehydrogenation of alkanes [33–35] and propene oxidation [36]. But in all cases, the suggested reaction mechanism involves lattice oxygen associated to the molybdenum ion, while the role of cobalt and other elements is to form the active phase and reoxidize the reduced molybdenum ions.

It is also known that isolated cobalt ions is well dispersed in CoO–MgO solid solutions may form O_2^- and superoxide adducts [37], although at rather low temperatures (77 K). At room temperature this species gives cleavage of the C=C double bond (therefore gives unselective electrophilic attack), but with toluene, oxidation of the Me group takes place [38]. In zeo-type matrices (CoAPO-11), upon adsorption of O_2 on H_2-pretreated sample (reduction generates an active Co^{2+} species), a paramagnetic peroxo-type species forms which at relatively high temperatures (above 300 °C) converts into inactive Co oxo species [39,40]. Cobalt alkyl peroxo complexes have been suggested as intermediates in the industrial oxidation of hydrocarbons with cobalt catalysts in the liquid phase [1–4]. Heterogenized Co bimetallic complexes anchored to silica has been shown to form peroxo complexes by exposure to an oxygen atmosphere at room temperature and this peroxo compound has been shown to be the active species in cyclohexene selective oxidation at 170 °C [41]. The formation of peroxo-Co dimer complexes is well known [42], but indication on the thermal stability of these species is very limited. It is also known that cobalt ion-exchanged X and Y zeolites are active in the gas-phase oxidation of benzyl alcohol to benzaldehyde and that a relationship exists between amount of O_2 uptake from the sample and catalytic activity [43].

Therefore, there are a series of very preliminary indications suggesting that also in the heterogeneous gas-phase oxidation peroxo or radical-type oxygen species may form over cobalt ions well dispersed in a structured matrix and that these species may be able to give selective oxidation of alkylaromatics, although probably in a limited temperature range and under particular reaction conditions. On the other hand, the proof of this concept may demonstrate that also in the selective oxidation on oxide-type catalysts under relatively mild reaction conditions radical-type reaction mechanisms of selective oxidation can be possible, e.g. not only at high temperature where mixed homogeneous–heterogeneous mechanisms of oxidation involving radical species are well established [44].

The scope of the work reported here was to make an exploratory study to analyze the possibility that Co-based solid catalysts can be selective in the oxidation of toluene and make some preliminary attempt to analyze whether or not radical- or peroxo-type mechanisms analogous to those active in liquid-phase selective oxidation could be also present in the gas-phase selective oxidation.

2. Experimental

2.1. Preparation of the catalyst

Co–Al-hydrotalcite (HT Co:Al = 2:1 and 3:1) samples were prepared by co-precipitation at 60 °C and at a controlled pH of 9.5–10.0 using as precipitation agent Na_2CO_3. Co(II) and Al(III) nitrates were used as the starting compounds. During precipitation, the pH was kept constant by adding NaOH 3M or HNO_3 conc. The obtained hydrotalcite-like precursors, after aging at 60 °C for 20 h, have been washed with hot distilled water until complete Na^+ elimination. The precipitates were then dried at 90 °C

overnight and subsequently calcined at 550 °C. X-ray powder diffraction patterns (XRD), IR and UV–vis–NIR diffuse reflectance characterization of the HT Co–Al-derived samples indicate the presence of a crystalline Co-spinel phase with surface area of about 80 m^2/g in both samples and the presence of small nanosized Co-oxide particles on the surface.

Co supported on alumina (Co/Al_2O_3) with a cobalt loading of 20 wt.% was prepared by wetness impregnation with an aqueous solution of Co-acetate using a commercial γ-Al_2O_3 support (PURALOX SCCa 30/200, from Sasol) having a surface area of 150 m^2/g. No significant change in the surface area was noted after addition of cobalt. The sample, after drying, was calcined at 550 °C (6 h). XRD characterization shows the presence of low crystalline γ-Al_2O_3 and broad reflections for Co-oxides, indicating the high dispersion of cobalt ions and/or the presence of amorphous Co-oxides.

Co/SBA-15 was prepared by incipient wet impregnation of SBA-15, the latter synthetized with a modification of the procedure described by Zhao et al. [45]. The starting material for the wet-impregnated catalyst was a SBA-15 obtained by self-assembly on a Pluronic P123 triblock polymer (PEO-PPO-PEO, Aldrich). After synthesis of the ordered mesoporous material and careful removal of the polymer by slurrying with ethanol under reflux conditions, the resulting white product was dried and then calcined at 500 °C for 6 h. Cobalt was then introduced on the SBA-15 channels by impregnation with an aqueous solution of $Co(CH_3COO)_2{\cdot}4H_2O$ to obtain a Co loading of 9%. This sample was dried to remove the imbibed liquid. The impregnated support was activated by calcination at 550 °C (5 h, 5 °C/min). XRD, SEM and TEM characterization indicates the presence of a well-ordered SBA-15 phase without the presence of crystalline Co-oxide phases or aggregates on the external surface.

$LaCo_{0.67}Mn_{0.33}O_3$ has been prepared by coprecipitation using La^{3+}, Co^{2+} and Mn^{2+} nitrates, washing, drying and calcination as for above samples. The surface area was 3 m^2/g and XRD characterization shows the presence of an orthorhombic perovskite structure [46]. No evidences have been obtained about the presence of other crystalline phases. The amount of cobalt in this sample, determined by XRF, was 16 wt.%.

2.2. Reactivity tests

Initial screening tests were carried out using a linear increase of the reaction temperature (from 90 to 300 °C at a rate of 70 °C/min, then an isotherm at 300 °C for 5 min, and a further increase up to 450 °C at a rate of 10 °C/min) in a home-made flow reactor apparatus for temperature-programmed reactivity tests. A mixture of toluene/oxygen/helium (composition 2.3% toluene, 10% O_2, remaining helium) was feed to the catalyst monitoring on-line the reagents and products formation by a mass quadrupole detector (mass 18 for H_2O, 28 for $CO(N_2)$, 32 for O_2, 44 for CO_2, 79 for benzyl alcohol, 91 for toluene, 105 for benzaldehyde, 122 for benzoic acid). The amount of catalyst (in the form of powder with mean dimensions of 0.1–0.2 mm) used in these tests was 0.5 g and the spatial velocity was 12,000 h^{-1}. The same apparatus was also used to preadsorb toluene or oxygen at 100 °C, monitoring then the products desorbing from the catalyst in a pure helium stream.

Transient reactivity tests were made in a second flow fixed-bed reactor apparatus. The feed could be sent either to the reactor or to a bypass for its analysis. The feed from the reactor or the bypass could be sent to a vent or to one of two parallel absorbers containing a solvent (plus calibrated amounts of an internal standard) cooled at about −15 °C in order to condense all organic products. The line to the absorbers was heated at about 200 °C in order to prevent condensation of the products. The vent, after condensation of the organic products, was sent to a sampling valve for analysis of the residual gas composition using a gas chromatograph (GC) with a thermoconductibility detector (packed column 60/80 Carboxen 1000). The solution in the absorbers was instead analyzed with a second GC with a flame ionization detector for organic products (fused silica wide-bore column). Products identification was made using another GC with mass quadrupole detector. The space-velocity was similar to those of the screening tests, but the feed composition was 10.4% toluene, 5% O_2, and the remaining helium. The temperature in these tests was 254 °C, corresponding to the maximum formation of benzaldehyde observed in the preliminary screening tests. The change of catalytic performances as a function of the time-on-stream was evaluated during these tests. No pretreatment was made to the catalysts before the tests.

The same apparatus was also used to analyze the transient catalytic behavior in the absence of oxygen in the feed and to evaluate the performances when CO_2 (1%) was added to the feed without modifying the composition of the other reactants.

2.3. Characterization

The BET surface area was measured using N_2 sorption at 77 K. Prior to the experiments, the samples were outgassed at 120 °C for 3 h. X-ray powder diffraction patterns were collected using Cu Kα radiation, on a Ital-Structures XRD diffractometer. Thermogravimetric analyses were carried out using a TGA Q50 Thermal Analyzer (TA Instruments, Inc.). Measurements were made in a flow of air or N_2 (60 cm^3/min) with a heating rate of 10 °C/min.

3. Results and discussion

3.1. Temperature-programmed reactivity tests

For the initial screening tests, four types of different classes of Co-based catalysts have been selected:

(i) Co:Al mixed oxides obtained by thermal treatment starting from hydrotalcite (HT) precursors, because it is known that well-dispersed Co^{2+} ions are present on the surface of the spinel-like oxide in close interaction with nanosized Co-oxide [47–49] and that these catalysts are active in the liquid-phase oxidation by molecular oxygen of benzyl alcohol to benzaldehyde [50,51]. Two samples have been prepared with Co:Al ratio of 2:1 and 3:1. They will be indicated as HT Co:Al = 2:1 and HT Co:Al = 3:1, respectively.

(ii) Cobalt oxide (20 wt.%) supported on alumina, because this is an obvious reference to understand differences between special cobalt species which may form upon thermal transformation of the Co–Al-HT samples and supported species. This sample will be indicates as Co/Al_2O_3 hereinafter.

(iii) Co well dispersed in an ordered mesoporous matrix (SBA-15), because it is known that (a) these mesoporous materials allow a high dispersion of Co ions [52] (better than on MCM-41 samples and having in addition also a better thermal stability), (b) do not show problem of rate of diffusion/back-diffusion from the inner pores as in microporous materials (mean dimension of the pores of mesoporous ordered materials is significantly larger than in MeAPO materials; a low rate of back-diffusion from micropores was already demonstrated to lower the selectivity in alkylaromatic selective oxidation [26]), and finally (c) have been reported to show interesting performance in *p*-xylene liquid-phase oxidation [53]. This sample (9 wt.% of cobalt) will be indicated as Co/SBA-15 hereinafter (for higher amounts cobalt-oxide particles started to be detected by TEM on the other surface of SBA-15 mesoporous crystals [54]).

(iv) a Co–Mn perovskite, because also in this case Co^{2+} species are present on the surface [55] and it has recently reported that similar catalysts are active in the liquid phase for the selective oxidation of alkylaromatics to benzaldehyde [56]. This sample, having the following composition $LaCo_{0.67}Mn_{0.33}O_3$ will be indicated as $LaCoMnO_3$ hereinafter.

Reported in Fig. 1 is the catalytic behavior of these samples during temperature-programmed reactivity tests in a flow of toluene/O_2/helium. Top graph reports the normalized (with respect to helium) ion current of the mass 106 (benzaldehyde) and bottom graph the corresponding normalized ion current for mass 44 (CO_2). Co/Al_2O_3, Co/SBA-15 and $LaCoMnO_3$ samples show an activity which decreases in the same order with a light-on beginning at about 300 °C for Co/Al_2O_3, 380 °C for Co/SBA-15 and 420 °C for $LaCoMnO_3$, respectively. In all cases a jump increase of the toluene conversion was noted. No benzaldehyde or other products of partial oxidation formation (apart from little amounts of CO) were detected on these catalysts.

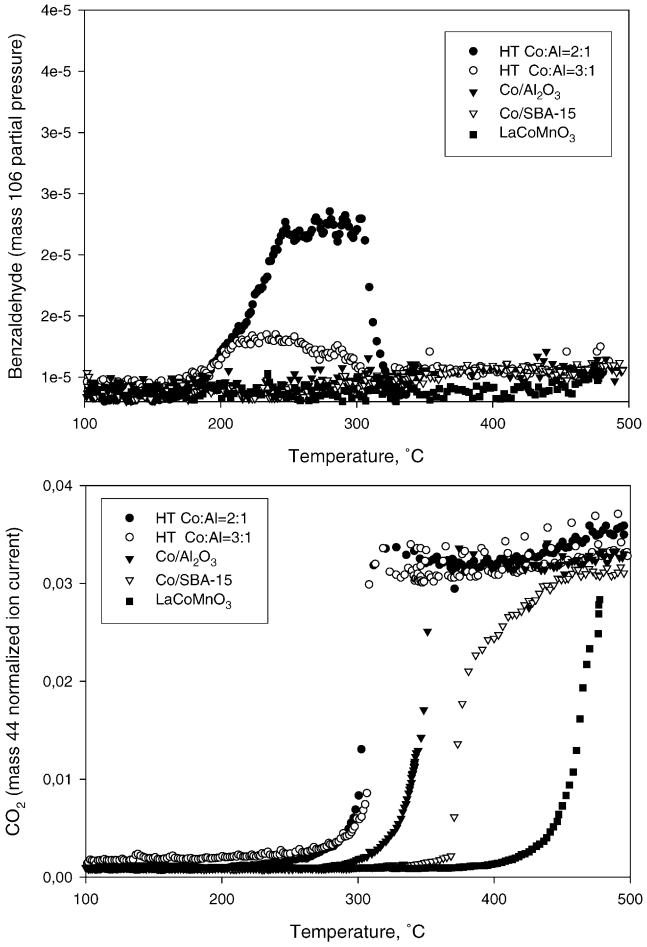

Fig. 1. Catalytic behavior of Co-based samples (see text) during temperature-programmed reactivity tests in a flow of toluene/O_2/helium (2.3:10.0:87.7). Top graph: normalized (with respect to helium) ion current of the mass 106 (benzaldehyde). Bottom graph: normalized ion current for mass 44 (CO_2).

On the contrary, hydrotalcite-derived samples show the formation of benzaldehyde (although in low amounts) at low temperature, in the region just below the jump increase of the CO_2 signal near to 300 °C. No relevant differences in the CO_2 formation (and toluene conversion) were noted between the two samples with Co:Al ratio of 2 and 3, but the latter forms significantly lower amounts of benzaldehyde.

Fig. 2 shows in more detail the behavior observed for HT Co:Al = 2:1 during temperature-programmed reactivity tests. For reasons of clarity, the signal of CO_2 (no CO was observed on these samples) is omitted, but corresponds to that already reported in Fig. 1. At a temperature of about 180 °C the signal of toluene started to decrease and similarly the signal of O_2, while a maximum in the formation of H_2O was noted. In correspondence, the signal of benzaldehyde began to increase reaching nearly plateau in the region between about 250 and 300 °C. A further increase in the temperature above 300 °C caused the drastic decrease of benzaldehyde formation and the jump of toluene and oxygen conversion (decrease of their signal). As shown in Fig. 1

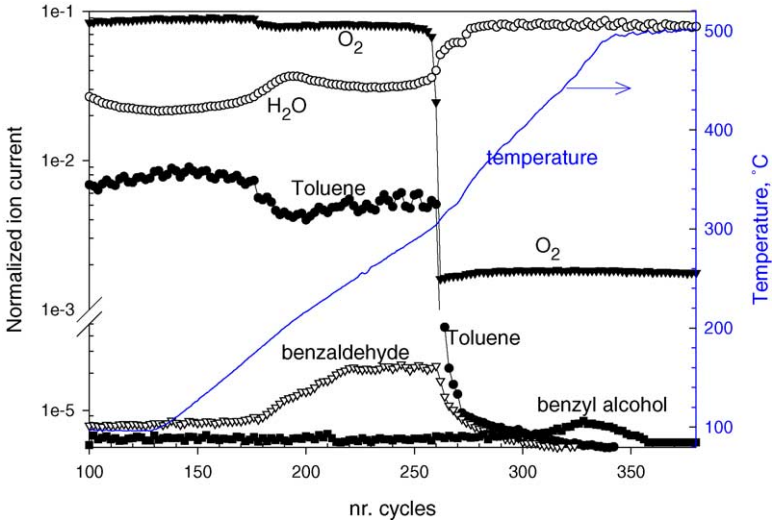

Fig. 2. Catalytic behavior of HT Co:Al = 2:1 during temperature-programmed reactivity tests in a flow of toluene/O_2/helium.

(bottom graph), there is a corresponding step-like change in the formation of CO_2. It may be noted that at higher temperatures (near to 450 °C), when complete conversion of oxygen causes possibly a partial reduction of the catalyst, a very small peak in the formation of benzyl alcohol is detected. The formation of benzyl alcohol was never observed in allylic-type selective oxidation catalysts for toluene gas-phase oxidation and suggests that may be an intermediate to benzaldehyde on these Co-based catalysts. No benzoic acid formation was detected in all the range of temperatures examined.

3.2. Flow reactor transient reactivity tests

In order to confirm the results obtained with the temperature-programmed reactivity tests, the performances of HT Co:Al = 2:1 sample were evaluated at fixed temperature in flow reactor experiments, analyzing the change of the catalytic behavior as a function of the time on stream. The temperature of the tests was 254 °C, corresponding to the maximum benzaldehyde formation during temperature-programmed reactivity tests. Three type of experiments were made using different feeds: (i) a toluene/O_2/helium mixture, (ii) the same as the former one, but omitting O_2 and (iii) the same mixture as the first one, but partially substituting helium with CO_2 (1% in the feed). The results are shown in Fig. 3. Being present some adsorption of toluene and of the reaction products during these tests (see later), the selectivity in these experiments was calculated on the basis of the products of reaction detected in the outlet stream from the reactor (benzaldehyde and CO_2 only). However, selectivity is not reported for the tests in the presence of CO_2 co-feeding, due to the large experimental error in determining carbon dioxide formation as an addition to CO_2 already present in the feed.

The experiments co-feeding CO_2 are motivated from recent results indicating that (i) in the gas-phase oxidation with O_2 of alkylaromatics to aldehydes over Fe/Mo/zeolite catalysts [57] carbon dioxide promotes the reaction by forming surface peroxocarbonate species which were suggested (although not demonstrated) to be the active species in the reaction and (ii) carbon dioxide also promotes the reaction in the liquid-phase oxidation using Co/Mn/HBr homogeneous catalysts by forming a cyclic peroxocarbonate complex which catalyzes the hydrogen abstraction (rate-determining step) [58]. Peroxocarbonate surface species are known to be selective in hydrocarbon oxidation by one- or two-oxygen transfer depending on the reaction conditions [59] and therefore may play a role in stabilizing surface adsorbed oxygen species. Furthermore, it is known that mixed oxides derived from hydrotalcite materials adsorb CO_2 reconstructing locally the hydrotalcite-like structure (‘‘memory effect’’) [60] and therefore it is possible that HT Co:Al catalysts coordinate strongly carbon dioxide, possibly forming peroxocarbonate surface species by reaction with O_2.

The data reported in Fig. 3 show the following results:

1. The initial formation of benzaldehyde observed using a mixture of toluene/O_2/helium as the feed was relatively high. Benzaldehyde was essentially the only product of reaction revealed and therefore the selectivity (based on the sum of the reaction products) was nearly 100% (based on the sum of the reaction products). However, a fast decline of the benzaldehyde productivity was noted during the first hour of time-on-stream. After about 2 h, also the selectivity to benzaldehyde significantly drops. It should be noted that the initial high selectivity to benzaldehyde may be an apparent effect (or at least the effective selectivity may be lower) due to the possible adsorption of the CO_2 formed during the reaction by the catalyst itself. Temperature-programmed reaction tests indicate that CO_2 can be adsorbed by the HT Co:Al = 2:1 catalyst, but it is difficult to estimate its amount deriving

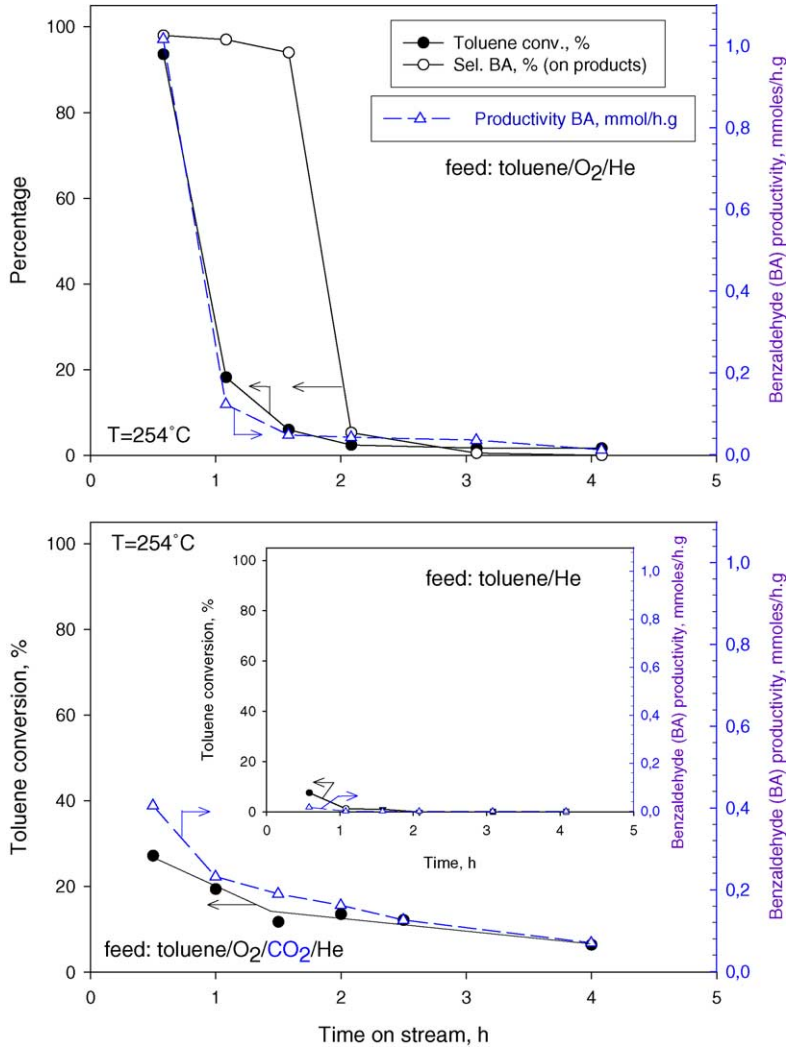

Fig. 3. Catalytic behavior of HT Co:Al = 2:1 at 254 °C in flow reactor experiments as a function of the time-on-stream. Top graph: feed of toluene/O_2/helium (10.4:5.0:84.6); bottom graph: feed of toluene/O_2/CO_2/helium (10.4:5.0:1.0:83.6). Inset in the bottom graph: toluene/helium (10.4:89.6).

from toluene combustion, because CO_2 is always present in traces in the feed.

2. In the absence of oxygen in the feed, benzaldehyde (or other products of reaction) is not detected, even at the beginning of the reaction. Tests were also made analyzing the transient reactivity by the mass quadrupole detector (which allows faster time response), but toluene was found to be not oxidized by the HT Co:Al = 2:1 catalyst in the absence of oxygen in the gas phase. The results confirmed the data reported in Fig. 3. Finally, a last attempt was made by analyzing the species which desorb from the catalyst during temperature-programmed desorption (TPD) runs in helium or He/O_2 flow after adsorbing toluene at 100 °C on the HT Co:Al = 2:1 catalyst. Data confirmed that no oxidation of adsorbed toluene occurred without the presence of gas-phase O_2. However, in the latter case the adsorbed toluene is oxidized to carbon oxides. These results pointed out that lattice oxygen is not involved in the reaction, and that possibly adsorbed oxygen species give rise to the selective oxidation. Toluene adsorption competes on the same sites and therefore its preadsorption inhibits the formation of these active oxygen species. As a consequence, benzaldehyde was not detected in the experiments of toluene adsorption at 100 °C and TPD in a flow of He/O_2; only carbon oxide were detected, because other adsorbed oxygen species are involved in their mechanism of formation. This interpretation may also explain why a fast decay in the productivity to benzaldehyde during flow reactor transient reactivity tests (Fig. 3, top graph) was observed. The stronger adsorption of toluene (or of the products of reaction) on the catalyst inhibits the further formation of these selective adsorbed oxygen species responsible for the benzaldehyde formation. This could explain also the drastic lowering of the selectivity.
3. The presence of 1% CO_2 in the feed together with O_2 decreases the initial productivity to benzaldehyde as well

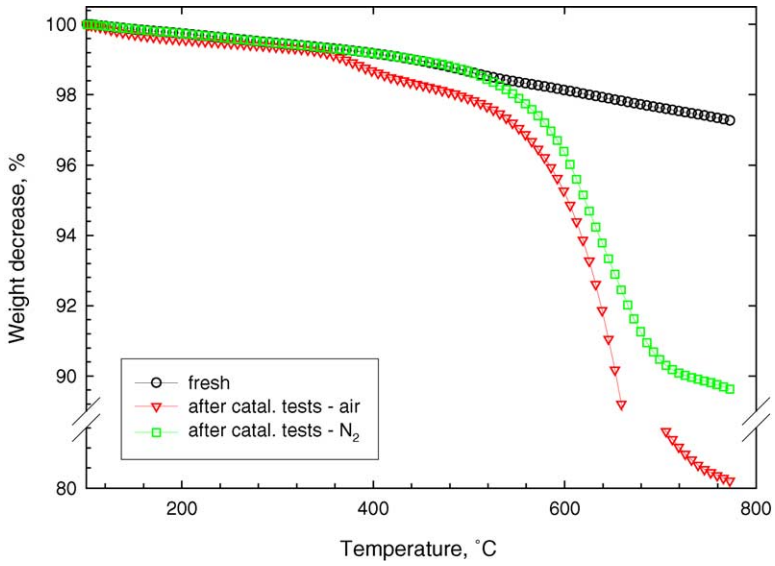

Fig. 4. Thermogravimetric tests of fresh HT Co:Al = 2:1 (in air) and of the same sample after catalytic tests (as in Fig. 3, top graph). The latter tests were made in a feed of air or N_2.

as the conversion of toluene, but markedly decreases also the rate of deactivation. The integrated benzaldehyde productivity in the presence and absence of CO_2 in the feed is analogous (around (6–7) $\times$ 10^{-4} moles benzaldehyde per g catalyst). Characterization data of the HT Co:Al = 2:1 sample indicate the presence of a spinel-like phase and of cobalt oxide well dispersed on the former phase. For a surface area of 80 m^2/g and a spinel phase ($CoAl_2O_4$), the number of surface Co^{2+} ions would be about 2 $\times$ 10^{-4} moles per g catalyst [61]. This value is comparable with the total amount of benzaldehyde formed, taking also into account that in HT Co:Al = 2:1 there is an excess of cobalt with respect to the stoichiometric value to form the spinel-like phase. This excess of cobalt is present both as nanosized cobalt oxide and as well dispersed cobalt ions in interstitial positions in the spinel-like phase [62]. Therefore, the number of total moles of benzaldehyde formed either in the presence or absence of CO_2 in the feed is consistent with a hypothesis that the active sites may be oxygen chemisorbed on surface-exposed Co^{2+} ions of the spinel phase probably located at the interface with nanosized Co-oxide particles. This agrees with recent indications showing the high oxygen carrier capacity of CoO_x/$CoAl_2O_4$ catalysts [63]. However, the turnover number of these sites is quite low and for this reason there is a fast deactivation (Fig. 3, top graph) due to the transformation of the sites to inactive one (as discussed in the introduction transformation of peroxo species to inactive Co oxo species) and/or to the formation of strongly adsorbed species which block activity of the sites. The presence of CO_2 in the feed either competes with the adsorption of these species or react with chemisorbed oxygen to form peroxocarbonate surface species less active, but more stable and less sensible to above deactivation mechanisms. For this reason, a lower initial activity together with a lower rate of deactivation (compare top and bottom graphs in Fig. 3) was observed when CO_2 was co-feeded.

3.3. Temperature-programmed desorption tests

Reported in Fig. 4 are the temperature-programmed gravimetric (TG) tests on HT Co:Al = 2:1 sample before and after the catalytic tests (as in Fig. 3, top graph). Tests in air show a first minor weight decrease in the 400–600 °C temperature range (less than 1%), while there is a drastic weight decrease in the 600–700 °C range corresponding to about 15–20 wt.% of change. The weight change corresponds to CO_2 evolution, but could be observed also feeding N_2 instead of air to the TG apparatus, although the weight decrease was about half in the absence of O_2. This indicates that this weight change corresponds at least in part to the desorption of CO_2 strongly bound to the catalyst (in agreement with the results on the CO_2 adsorption on hydrotalcite adsorbent [60,64]), but in part also to the combustion of organic adsorbed species. Reasonably the first small weight decrease in the 400–600 °C temperature range is due to the combustion of toluene chemisorbed on the catalyst, but the more intense weight decrease above 600 °C to the combustion of stronger chemisorbed species such as acids [60]. The second combustion step occurs together with the desorption from the catalyst of the strongly chemisorbed CO_2. Therefore, these results confirm that probably CO_2, if formed during the initial part of the flow reactor transient reactivity tests (Fig. 3), could remain adsorbed on the catalyst, but also indicate that probably the deactivation of the catalyst is due (at least in part) to the formation of products such as acids which block site reactivity.

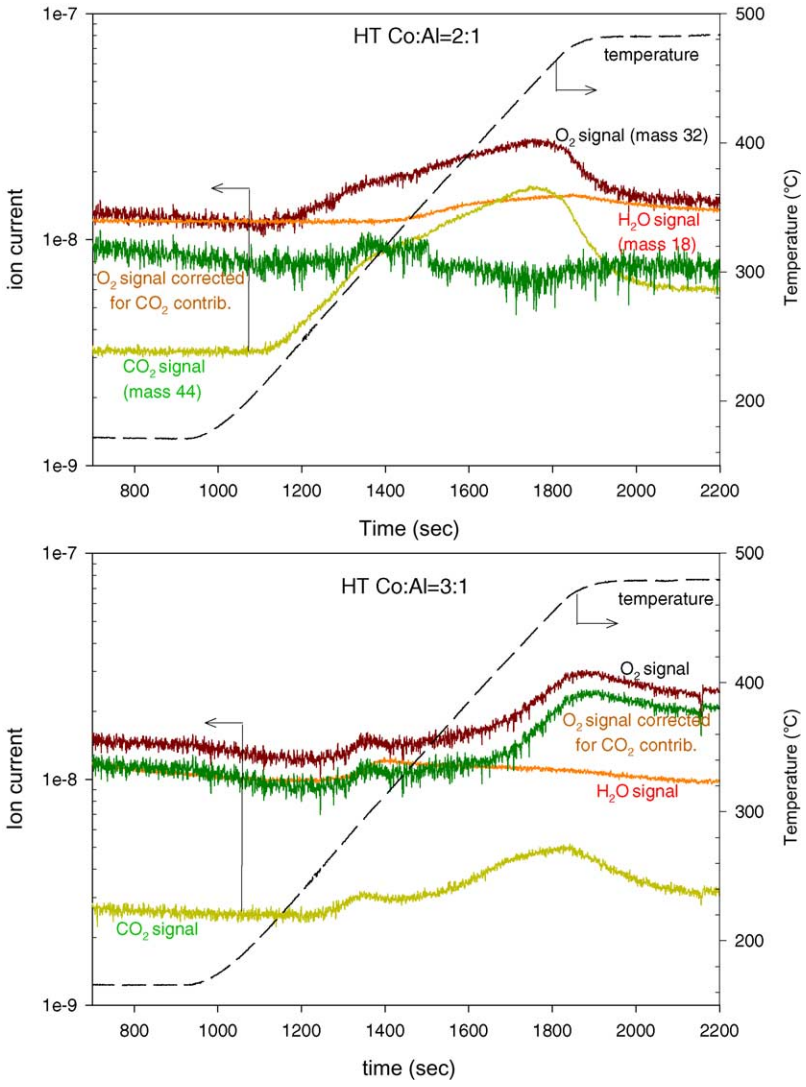

Fig. 5. Temperature-programmed desorption curves in He flow of HT Co:Al = 2:1 (top graph) and HT Co:Al = 3:1 (bottom graph) samples after the pretreatment procedure described in the text.

Reported in Fig. 5 are the temperature-programmed desorption curves made using the following pretreatment procedure: (i) the catalyst is treated in helium at 500 °C (2 h), (ii) cooled down to 150 °C in a helium flow, and (iii) saturated with air at this temperature. Then, the temperature is linearly increased from 150 to 480 °C monitoring the species which desorb from the catalyst by mass spectrometer. The objective was to monitor the possible desorption of adsorbed oxygen from the catalyst. In these tests, desorption of CO_2 from the catalyst was always observed. This desorption occurs in two steps, one at around 280 °C and a second around 450 °C. This is due to either incomplete CO_2 desorption during pretreatment at 500 °C and/or to partially capture again of CO_2 (present always in traces in the feed) during cooling down of the catalyst in helium flow. Carbon dioxide, besides to the main mass at 44, has a component also at 32 (peak of O_2) which partially mask the results. Therefore, a first run feeding CO_2 in helium was made, estimating the ratio between the peaks at mass 44 and 32. Verified that this ratio remains constant during the temperature-programmed experiments, the relative contribution of CO_2 to the mass 32 was subtracted electronically to determine the corrected mass intensity for the signal of O_2. Reported in Fig. 5 are the original signals for mass 44 (CO_2) and 32 (O_2) and the correct mass intensities determined for oxygen. The experiments were made on the HT Co:Al = 2:1 and Co:Al = 3:1 samples. The latter also gives some small amounts of benzaldehyde, but is less selective (Fig. 1).

In both cases a weak peak for O_2 (corrected signal for CO_2 contribution) could be observed centred to a temperature of about 260 °C (the same of the maximum in benzaldehyde formation; see Fig. 1). In HT Co:Al = 3:1 a second stronger signal at higher temperature (near to 480 °C) was observed which corresponds to the reduction of

Co_2O_3 to CoO. This second peak is clearly absent in HT Co:Al = 2:1, indicating that this spontaneous reduction process is absent in this sample. Reasonably this could be the reason of the lower selectivity of HT Co:Al = 3:1.

More questionable is whether or not the small peak near 260 °C could be really associated to active adsorbed oxygen species for benzaldehyde formation. The peak is rather small and obtained from the correction of the signal at mass 32, although precautions have been taken to minimize the possible sources of error. Nevertheless, a margin of error is possible. Therefore, it is more correctly consider this peak as an indication of the possible presence of adsorbed oxygen species which need further studies to be demonstrated.

4. Conclusions

The objective of the study reported here was an exploratory investigation made in order to analyze whether or not (i) cobalt catalysts could be active in the selective toluene to benzaldehyde oxidation and (ii) a different reaction mechanism from the more known redox Mars–van Krevelen mechanism (oxidation by lattice oxygen and reoxidation of the reduced catalyst) could be eventually responsible of the catalytic performances of these catalysts.

The answer to the first question is that effectively cobalt catalysts not containing other transition metals such as Mo or V can be active and selective in benzaldehyde synthesis, although in a very limited temperature range and there is a fast deactivation. The screening was limited to few classes of materials, but the results suggest that this is not a general property of (supported) cobalt ions, but is instead limited to specific sites present in specific samples. Only one sample between those tested (HT Co:Al = 2:1) was found to be active, but changing the Co:Al ratio the selectivity decreases. As far as we known this is the first example of gas phase heterogeneous Co-based catalyst shown to be active in the reaction and which activity could be associated to cobalt and not to other transition metals such as molybdenum and vanadium.

Regarding the reaction mechanism, there are a series of evidences indicating that adsorbed oxygen, possibly peroxo-type, are present on the catalysts and responsible of the catalytic behavior, even though should be remarked that further studies are necessary. As a working hypothesis, it may be tentatively suggested that the cobalt species responsible of the behavior are Co^{2+} ions on the surface of the spinel-like phase probably near to supported nanosized cobalt oxide particles. Although the results are preliminary, this point evidences that radical- or peroxo-type surface mechanisms of selective oxidation are possible also in the gas-phase oxidation of alkylaromatics, opening some new direction of research. The observed small formation under O_2-deficient conditions of benzyl alcohol as product of reaction (Fig. 2) is consistent with a peroxo-type mechanism, because this is the expected intermediate differently from the allylic-type Mars–van Krevelen reaction mechanism.

A fast deactivation of these sites was observed and therefore a way to overcome this issue should be found. Data pointed out that at least in part the deactivation is due to the formation of strongly adsorbed species (possibly acid-type) which can be oxidized also above 600 °C, but other additional (irreversible) deactivation mechanisms cannot be excluded. Toluene competitive adsorption as well is also present, although toluene as such (e.g. without transformation) desorbs at relative low temperature (200–300 °C) on these catalysts and therefore it is not probably a main reason of deactivation. However, further investigations are necessary to better understand the reasons of deactivation. When CO_2 is co-feed, a stabilization of these sites (tentatively by forming peroxo carbonate species) is possible with a reduction of the deactivation rate. But being also reduced the initial activity (reasonably due to a competitive chemisorption of CO_2) of the integral amount of benzaldehyde formed during the reaction (Fig. 3) is not increased.

In conclusion, this contribution indicates that even non-classical selective oxidation catalysts such as Co–Al containing mixed oxides derived from hydrotalcite precursors (usually known as combustion catalysts for toluene [65]) may be selective in benzaldehyde synthesis from toluene under particular conditions, even if not of applicative interest. It is also suggested that these catalysts may show a reaction mechanism which is the equivalent in the gas-phase oxidation to that present in the liquid phase, e.g. involving radical- and peroxo-type species. This result could be relevant for the application of these solid catalysts to other type of selective oxidation reactions and/or to other type of reaction media (e.g., supercritical fluids).

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