

Room temperature oxidation of formaldehyde on Pt-based catalysts: A comparison between ceria and other supports (TiO₂, Al₂O₃ and ZrO₂)

Sara Colussi^{a,*}, Marta Boaro^a, Loredana de Rogatis^a, Alfonsina Pappacena^a, Carla de Leitenburg^a, Jordi Llorca^b, Alessandro Trovarelli^a

^aDipartimento di Chimica, Fisica e Ambiente, Università di Udine, via del Cotonificio 108, 33100 Udine, Italy

^bInstitut de Tècniques Energètiques and Centre for Research in Nanoengineering, Universitat Politècnica de Catalunya, 08028 Barcelona, Spain

a b s t r a c t

Platinum-based catalysts for the room temperature removal of formaldehyde are prepared on ceria and other supports (TiO₂, Al₂O₃ and ZrO₂) for comparison, starting from chloride and nitrate precursors. The behaviour towards formaldehyde adsorption and oxidation is evaluated by means of temperature-programmed desorption (TPD), temperature-programmed oxidation (TPO) and catalytic tests. The results indicate that the catalytic performances are affected by Pt oxidation state, which, in turn, strongly depends on the properties of the support. In order to obtain high HCHO conversions, the support should guarantee the accessibility to metal active sites as well as affinity for water. Moreover, to avoid Pt partial oxidation, non-reducible oxides are preferable to reducible ones. © 2015 Elsevier B.V. All rights reserved.

1. Introduction

Formaldehyde is regarded as one of the major indoor pollutants and has attracted wide attention in recent years due to its noxious effects on human health [1,2]. Its primary use is for the production of adhesive resins (i.e. with urea, phenol and melamine), which accounts for more than half of formaldehyde consumption. These resins are largely employed in woodworking industries for the manufacturing of pressed wood panels like particleboard, medium density fibreboard (MDF) and plywood, which, in turn, are widely used as building, furnishing and decorative materials. This ubiquitous presence results in high human exposure to formaldehyde emissions, and it is well known that acute exposure to HCHO causes irritation of eyes and upper airways [3] while long-term indoor exposure, even to few ppm of this aldehyde, is associated with a growing incidence of a variety of respiratory cancers [4]. Therefore, its complete elimination or, at least, its abatement below the threshold limits for dwellings and work places established by new environmental regulations is of paramount interest for the improvement of our health and life quality. Essentially, there are three ways to reduce the formaldehyde concentration in indoor air as well as other VOC emissions: the first is controlling and eliminating the emission source by using low-emission building materials ('source control'), the second is by reducing pollutant concentrations with fresh outdoor air by natural and mechanical ventilation ('dilution control'), the third strategy involves cleaning indoor air by mechanical air cleaning devices or decomposing agents ('air-cleaning control') [5]. Among air cleaning methods, removal of HCHO by adsorbents has been extensively studied [6–8], and although these materials can successfully reduce indoor formaldehyde concentration, they are effective only for a short period due to their limited sorption capacity. On the other hand, heterogeneous catalytic oxidation has shown to be one of the most promising processes for complete HCHO elimination [9]. While traditional filters or sorption materials only transfer the pollutant to another phase, catalytic oxidation can selectively transform formaldehyde into harmless final products, namely CO₂ and H₂O, at much lower temperature than those required in conventional

thermal oxidation. The ideal catalyst should be able to work at low temperatures (<100°C), possibly close to room temperature, and in the presence of moisture or other hazardous species that can lead to severe catalytic deactivation through the strong adsorption on the active sites. Furthermore, no other by-products (i.e. CO) should be released. The most common catalysts reported in literature for formaldehyde oxidation can be divided into two groups: (i) noble metal-based catalysts and (ii) transition metal-based catalysts [9]. Both noble and transition metals are typically dispersed on high surface area supports in order to increase the number of active sites and to enhance gas-solid interaction. Supported noble metals have been proved to be promising catalyst for HCHO oxidation because of their great activities at low temperature. According to the most recent literature findings, complete oxidation of formaldehyde can be achieved over supported Au, Pd and Pt catalysts already at room temperature [10–13]. Transition metal oxides are cheaper, but show somewhat lower efficiency since the temperature for complete conversion of HCHO is in general higher than for noble metals [14,15]. Some efforts have been made for the improvement of noble metal-based catalysts, for example by doping with alkali metals [16–19] and by tuning catalytic properties with different preparation methods leading to specific material structures and/or to the reorganization of the exposed metal surfaces [20–24]. Among the noble metals, platinum appears to be the most active, and many studies investigate its catalytic behaviour on different supports and with different reaction conditions [9]. Most papers are focused on Pt supported over TiO₂ [19,21,23,25–30], while other works considered iron [31], silica [32,33], ceria [34] and mixed oxides [32,35,36]. Huang et al. observed that the reduction with sodium borohydride was very effective for the catalytic activity of Pt supported on TiO₂ [28,37]. The same treatment was recently reported by Nie et al., who obtained the decomposition of formaldehyde at room temperature over both Pt/TiO₂ and structured honeycomb ceramic monoliths impregnated with ultra-low amount of platinum, indicating that the reduction itself seems the key parameter instead of the nature of the support [13,23]. In the work by Peng et al., that to our best knowledge, is the only one in which a comparison between platinum on different supports is carried out, the authors individuate Pt dispersion as the controlling factor for catalytic activity [32]. Within this complex scenario, our work is aimed at the investigation of the behaviour of platinum impregnated on different supports starting from two precursor salts (ex-chloride and ex-nitrate), in order to find the key parameters for the activity towards formaldehyde oxidation at low temperature. The catalysts (platinum on Al₂O₃, CeO₂, TiO₂ and ZrO₂) were deeply characterized and tested for HCHO interaction with the surface by temperature-programmed oxidation (TPO) and desorption (TPD). Catalytic tests for a preliminary evaluation of catalyst performances were also carried out.

2. Experimental

2.1. Catalysts preparation

Platinum was impregnated by incipient wetness technique on four commercial oxides (TiO₂ Degussa P25, Al₂O₃ and CeO₂, gently provided by Grace Davison and ZrO₂ Mel Chemicals) starting from two different precursors: H₂PtCl₆ · 6H₂O (Strem Chemicals, 99.9%) and (NH₃)₄Pt(NO₃)₂ (Aldrich, 99.995%), in order to obtain catalysts with a nominal loading of 1 wt.%. The supports were previously calcined at 500°C for 3 h in air, and after impregnation, the samples were dried overnight at 110°C and calcined at 500°C for 3 h. The powders were then crushed and sieved to collect the fractions suitable for the catalytic tests (≤250 μm).

2.2. Catalysts characterization

BET surface area, pore volume and an average pore diameter of the catalysts were measured by N₂ adsorption at liquid nitrogen temperature using a Tristar 3000 gas adsorption analyzer (Micromeritics). Approximately 150 mg of catalyst, previously degassed overnight at 150°C, were used for each analysis. The amount of Pt was determined by inductive coupled plasma (ICP-AES) on all samples. Powder X-ray diffraction (XRD) patterns of the catalysts after calcination were recorded with a Philips X'Pert diffractometer operated at 40 kV and 40 mA using nickel-filtered CuK α radiation. Spectra were collected using a step size of 0.02° and a counting time of 40 s per angular abscissa in the range of 20–80°. Temperature-programmed reduction (TPR) experiments were carried out in an AutoChem II 2920 analyzer (Micromeritics) on ~50 mg of the calcined materials in a conventional U-shaped quartz microreactor using a 5% H₂ in argon mixture flowing at 35 ml min⁻¹ (STP). For TPR measurements, the temperature was increased from ~50 to 800°C at a heating rate of 10°C min⁻¹. The samples were pre-treated at 500°C for 1 h in an air flow (50 ml min⁻¹) before the analysis. H₂ consumption was monitored using a thermal conductivity detector (TCD) as a function of temperature. Particle morphology and dispersion were analyzed by conventional bright-field transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images taken at different magnification. The microscope used was a JEOL 2010 operating at 200 kV and equipped with a field-emission gun. Samples were dispersed onto holey-carbon grids from alcohol suspensions.

2.3. Reactivity measurements

Temperature-programmed desorption (TPD) and oxidation (TPO) experiments were carried out in a conventional tubular fixed-bed reactor under atmospheric pressure. The sample ($\phi \leq 250 \mu\text{m}$) was loaded in a quartz microreactor (i.d. 4 mm) on a quartz wool bed. All TPD–TPO profiles were collected after exposure of the samples to an aqueous solution of formaldehyde (containing 24.5–25.0 wt.% HCHO without additional stabilizing agent) at room temperature (RT). The solution was fed with a Hamilton Gastight syringe using a INSTECH Model 2000 pump at a rate of ~0.090 $\mu\text{l min}^{-1}$ mixing it with flowing helium through a heated line (~150°C) to avoid condensation. The resulting total composition of the gaseous feed was HCHO/H₂O/He = 300 ppm/1500 ppm/balance He with a total flow rate of 60 ml min⁻¹, corresponding to a gas hourly space velocity (GHSV) of ~150,000 ml g⁻¹h⁻¹. In TPD experiments, the sample was exposed to the formaldehyde containing mixture and maintained at room temperature for 1 h, then the gas was switched to pure helium and the temperature was increased to 300°C at a heating rate of 10°C min⁻¹. In the case of TPO experiments, after exposure to the same gas mixture (HCHO/H₂O/He = 300 ppm/1500 ppm/balance He) at room temperature for 1 h, the feed was switched to a mixture of 1 vol% O₂ in helium with a total flow rate of 60 ml min⁻¹ and the temperature was increased up to 300°C (heating rate of 10°C min⁻¹). For both TPD and TPO, the reaction/desorption products were qualitatively recorded with a mass spectrometer (Omnistar QMS200, Balzers instrument) as a function of the temperature. Before TPD and TPO experiments, the calcined materials were treated under air flow at 500°C for 1 h (50 ml min⁻¹, 10°C min⁻¹) and then reduced in H₂(5%)/Ar at 300°C for 1 h (35 ml min⁻¹, 10°C min⁻¹). A blank test was carried out without catalyst and no adsorption/oxidation was observed. For the catalytic tests, the samples were exposed at 25°C to a reactant mixture having the following composition: HCHO/H₂O/O₂/N₂ = 100 ppm/500 ppm/20 vol.%/balance N₂ with a total flow rate of 300 ml min⁻¹. The catalysts were tested in fresh, reduced and regenerated form. The regeneration consisted in the oxidation of the used sample (in air at 500°C for 1 h, 50 ml min⁻¹, 10°C min⁻¹) followed by its in situ reduction (5 vol.% H₂ in Ar at 300°C for 1 h, 35 ml min⁻¹, 10°C min⁻¹). The concentration of reactants and products was monitored with an on-line FT-IR analyzer (MKS

MultiGas 2030) and the catalytic activity of samples was compared on the basis of HCHO conversion after 150 min. In order to guarantee a stable concentration of formaldehyde during the catalytic tests, HCHO was fed flowing nitrogen through the S. Colussi et al. / Catalysis Today 253 (2015) 163–171 165 Fig. 1. Schematic representation of the experimental setup for the catalytic activity tests (solid line: water for saturator and thermostatic bath; dotted line: heated line for reactants and products). formalin solution in a saturator. The complete scheme of the setup is reported in Fig. 1.

3. Results

3.1. Catalyst characterization

Surface area and elemental analysis of each sample is reported in Table 1. Compared to the bare oxides, TiO₂-, CeO₂- and ZrO₂-supported catalysts show a slight reduction of specific surface area after Pt impregnation, while the surface area is essentially the same for alumina-supported sample. The metal content is close to the nominal value of 1% for all catalysts. X-ray diffraction profiles of all calcined samples are reported in Fig. 2. Looking at the spectra of bare supports, it can be observed that titania (upper-left panel) is present in both anatase and rutile forms, while for ceria (upper-right panel), only the characteristic peaks belonging to the typical cubic form with Fm-3 m symmetry are observed. The theoretical value for complete Pt reduction, according to the metal loading, is 1.21 ml/g for PtO and 2.42 ml/g for PtO₂ detected. Zirconia (lower-left panel) shows the features of mono-clinic and cubic forms, and alumina presents the peaks belonging to cubic and hexagonal structures, typical of γ -alumina. In all samples, the structure of the supports is not changed by the impregnation of the noble metal, i.e. they retain their crystal forms and there is no evidence of sintering induced by the presence of platinum. Metallic platinum ($2\theta = 39.9^\circ$) is detected only on TiO₂ and Al₂O₃ and only on the catalysts prepared starting from nitrate precursors. HRTEM analysis of the reduced samples considered in this work is shown in Fig. 3. In all catalysts, Pt particles are very well-dispersed on the corresponding support. No Pt agglomerates or regions with different Pt particle sizes are present. From HRTEM, it is not possible to evidence a role of precursor on platinum clusters morphology. The average particle size and the particle size interval for 95% of all particles measured for each sample are summarized in Table 2. TPR profiles (not normalized) of the Pt-based catalysts are shown in Fig. 4. On all samples, except on Pt/Al₂O₃-N, H₂ consumption peak is observed pointing to the presence of some oxidized platinum. Quantitative results reported in Table 3 indicate that on samples prepared starting from chloride precursor, the amount of PtO_x species is slightly higher than that on samples prepared from nitrate salt. This is probably due to a simultaneous reduction of platinum during the decompositions of nitrates in the calcination step. On the contrary, the formation of species less prone to decomposition/reduction during calcination like oxychloroplatinum (PtO_xCl_y) might account for the higher amount of hydrogen consumption observed in TPR experiments [38]. By comparing the reducibility on the different supports, it can be observed that Pt reduction on TiO₂ starts at much lower temperature with respect to the other supports due to the higher dispersion of Pt on this oxide. On the other hand, the highest temperature of reduction is recorded on Pt/CeO₂-Cl. Moreover, ceria supported sample also exhibits the highest hydrogen consumption, clearly related to the simultaneous reduction of CeO₂ due to H₂ spillover [39].

3.2. Reactivity studies

As a first approach, the reactivity of the catalysts was studied in terms of surface interaction with formaldehyde by means of temperature-programmed desorption and oxidation experiments. Fig. 5 shows the TPD profiles of the bare supports that have been considered in order to take into account the contribution coming from the surface of the support itself. Formaldehyde desorption ($m/z = 29$ and 30) is detected on TiO₂ and Al₂O₃ supports with a maximum at about 100°C together with the signals related to HCHO

decomposition, namely CO and H₂, according to the following reaction: On alumina, a strong signal belonging to water desorption can be observed, with a sharp increase around 50°C and a subsequent stabilization above 150°C. This feature, likely due to the presence of water associated with the exposure of the powder to the formalin solution, is stronger than that on the other supports; this can be related to the higher surface area of Al₂O₃ that allows a higher adsorption of water together with the desorption of hydroxyl groups from the OH rich alumina surface. On CeO₂ and ZrO₂, the signals belonging to m/z = 29 and 30 are almost negligible, while both supports exhibit a strong peak from m/z = 28 between 230 and 300°C. On ceria, a peak for m/z = 44 is also observed in the same temperature range, which can be related to the decomposition of an intermediate (H₂CO₂) that has been reported to form during the interaction of formaldehyde with ceria surface [40–42]. This process involves the contribution from lattice oxygen of ceria, which can supply further oxygen to oxidize H₂CO₂ to formate at increasing temperature; formate species can eventually decompose into CO₂, CO and H₂. The addition of platinum on the supports radically changes TPD profiles, as it can be observed from Fig. 6a (referred to samples prepared from chloride precursor) and 6b (samples from nitrate precursor). A common feature of Pt-containing catalysts is the presence of CO₂ (m/z = 44) and H₂ (m/z = 2) signals, indicating the activity of these samples towards the water-gas shift reaction (CO + H₂O ↔ CO₂ + H₂). CO signal (m/z = 28) is, in general, more pronounced (on TiO₂ and Al₂O₃) and/or its desorption is completed at lower temperature (on ZrO₂ and Al₂O₃) than that on bare supports, pointing to the activity of platinum for HCHO decomposition. This is also confirmed by the presence of a H₂ desorption peak with maximum at about 80–100°C on titania in correspondence with CO peak. The same feature appears as a broad peak on alumina. This picture is slightly different when considering ceria-based samples, for which the differences between pure CeO₂ and Pt-containing catalysts are somehow less evident. The addition of Pt shifts the CO₂ desorption peak to lower temperature (~100°C for Pt/CeO₂-Cl and ~50°C for Pt/CeO₂-N) compared to the bare support. This can be due to the well-known catalytic activity of Pt-ceria systems for low-temperature water-gas shift reaction [43], or to a promotion of intermediates decomposition operated by platinum. Since no hydrogen is detected in the low temperature range, the latter explanation seems more likely. Moreover, no CO is detected in the whole temperature range and this can be due to the complete conversion to CO₂ or to a stronger adsorption of CO on the surface. When looking at the effect of the precursors on TPD profiles, it can be observed that this effect is relevant only for TiO₂ and CeO₂-based catalysts (i.e. reducible supports), while for ZrO₂ and Al₂O₃, the differences are almost negligible. In particular, on Pt/TiO₂-Cl (Fig. 5a), the low-temperature peaks of H₂, H₂O and CO are much less pronounced than those on Pt/TiO₂-N, while the peaks belonging to formaldehyde desorption (m/z = 29 and 30) are more evident. This is likely due to a higher degree of HCHO decomposition over Pt/TiO₂-N with respect to Pt/TiO₂-Cl. Moreover, for Pt/TiO₂-N, the presence of a shoulder in the low-temperature peaks of H₂, H₂O and CO can be attributed to the intermediates that have been reported to adsorb specifically over platinum [44]. In the case of ceria, CO₂ desorption starts earlier on Pt/CeO₂-N than on Pt/CeO₂-Cl, while HCHO ↔ CO + H₂ 168 S. TPD in He over the bare supports. On the latter, a stronger signal belonging to water desorption is observed. The different behaviour of ex-nitrates and ex-chloride samples can be related to the formation of oxychloride compounds that hinder oxygen exchange between metal and support, and consequently, the decomposition of HCHO [35]. In the case of CeO₂, residual chlorides might not only contribute to delay the reduction of Pt species (Fig. 4) and the decomposition of HCHO, but they can also migrate onto the support replacing the oxygen vacancies of ceria through the formation of CeOCl phase [45,46]. Furthermore, without pre-reduction in H₂, the trend in terms of products distribution and TPD peak position is similar (data not reported). Indeed, in this case, formaldehyde acts as a

reducing agent, as indicated by the colour change of the materials at the end of TPD experiment.

HCHO has also been reported in literature for Au-based catalysts [47]. In order to evaluate the interaction of HCHO with the catalyst surface in an oxidative environment, temperature-programmed oxidation experiments have been carried out. For bare supports, the mass evolution during the heating ramp is very similar to TPD experiments (Fig. 5); the only significant difference is the presence of CO₂ in the temperature range of 200–300 °C for TiO₂ and between 250 and 300 °C for ZrO₂ and Al₂O₃. On ceria, the peak belonging to CO₂ is more pronounced than in TPD analysis, and starts at slightly lower temperature. A completely different picture appears on platinum-containing samples. Fig. 7a shows the TPO profiles for catalysts prepared starting from chloride precursor. It is clear that the addition of platinum promotes the decomposition and oxidation of the adsorbed HCHO, since on these samples CO₂ evolution is recorded at lower temperature with respect to the bare supports together with an increase of the signal belonging to water (*m/z* = 18). In addition, no more formaldehyde is detected during TPO experiments differently from what was observed for TPD. Interestingly, on Pt/CeO₂-Cl, the maximum for CO₂ desorption is ~100 °C higher than that on the other supports. When looking at TPO profiles of samples prepared starting from nitrate precursor (Fig. 7b), it can be observed that the only significant difference is detected for Pt/CeO₂-N. On this catalyst, the peak of CO₂ is shifted to lower temperature with respect to Pt/CeO₂-Cl, being similar to that of other supports. As previously observed, the formation of cerium oxychlorides species could be responsible for the different behaviour of the two catalysts, in fact, the presence of these compounds affects the reducibility of ceria and metal/support interactions [48]. This, in turn, results in a peculiar contribution of ceria to the oxidation of formaldehyde (as it will be discussed in the following section). On the basis of the evidences collected during the characterization of samples, particularly following TPD and TPO experiments, we decided to investigate the catalytic behaviour of samples prepared from nitrate precursor. Preliminary results of catalytic tests carried out on all samples are reported in Fig. 8. As it can be seen in Fig. 8, HCHO conversion after 2 h test on all samples (black: fresh samples; grey: reduced samples and dotted: second test after ox-red). Colussi et al. / *Catalysis Today* 253 (2015) 163–171 observed, the reduced form of all samples is more active than the fresh one. Alumina-based catalyst is the most active, giving about 62% HCHO conversion after 2 h of test followed by Pt/ZrO₂ (~58%), Pt/CeO₂ (~38%) and Pt/TiO₂ (~22%). In a subsequent catalytic test performed on regenerated catalysts after an oxidation–reduction cycle (oxidation at 500 °C, reduction at 300 °C), a significant decrease in conversion is observed for alumina and zirconia-based samples, while no deactivation is detected for ceria and titania-based samples.

4. Discussion

The results obtained in this study allow to investigate the role of the support in the catalytic oxidation of formaldehyde over Pt-based catalysts. The supports considered in this work (Al₂O₃, ZrO₂, CeO₂ and TiO₂) are different in terms of acidity/basicity and redox properties. From Fig. 8, it is evident that platinum has a higher activity in metallic form (HCHO conversion is many times higher on reduced catalysts compared to the fresh ones), and in general, the reactivity of both reduced and fresh samples strongly depends on the type of support. Regarding the fresh (oxidized) catalysts, it is possible to correlate the catalytic activity with their redox behaviour. The temperature of H₂ consumption over the different Pt-supported catalysts in TPR experiments (Fig. 4, prepared from nitrate) follows the order Pt/Al₂O₃ < Pt/TiO₂ < Pt/ZrO₂ < Pt/CeO₂. The same trend is observed for the catalytic tests, suggesting that at low temperature, the redox properties of the support might have a detrimental effect by maintaining Pt in partially oxidized form. On the other hand, the same redox properties can play a positive role in the oxidation–reduction step. This is likely due to the establishment of a stronger metal–support interaction, which allows a better control of Pt sintering, especially, for the smallest platinum particles. The permanent deactivation of ZrO₂ and Al₂O₃ catalysts can be explained within this scenario as due to the

sintering of the smallest Pt particles, which in these samples, range between 1.7 and 2.7 nm. Also, the activity of reduced catalysts is clearly related to the nature of support, but apparently has no straightforward connection to TPD and TPO results. TPD profiles of bare supports (Fig. 5) suggest that the supports have different affinity and reactivity towards formaldehyde: Al_2O_3 and TiO_2 , which have acid properties, adsorb formaldehyde weakly. HCHO release occurs in molecular form at low temperature (80–100°C), along with a partial decomposition. CeO_2 and ZrO_2 , which are more basic, form stable intermediates that decompose at temperatures higher than 250°C. In the case of CeO_2 , it is reported that the formation and stabilization of intermediates, such as dioxymethylene (CH_2O_2) and formate species is attributable to the redox properties of the oxide [41]. The same behaviour is observed for the corresponding supported catalysts (Fig. 6b), where platinum promotes the oxidation of intermediates to CO_2 . In this case, it is worth noting that the Pt/ CeO_2 -N catalyst is the only one that is able to produce CO_2 at temperature lower than 100°C. This is due to the capability of the support to provide the extra oxygen necessary to the oxidation of formate species. In oxidizing environment (TPO experiments, Fig. 7b), despite the different affinity of the supports for HCHO and the different type of intermediates, the reactivity at low temperature is indeed governed by the processes activated over platinum. In fact, it is reported that platinum can promote the oxidation of adsorbed intermediates by providing activated oxygen to the surface of catalyst [44]. In a general scheme of reaction at room temperature, formaldehyde can decompose on the catalyst surface to produce different intermediate species, such as methoxide (CH_3O), poly(oxyethylene) (CH_2O) and dioxymethylene (CH_2O_2). These species can be oxidized to formates that, in turn, decompose to H_2O and CO_2 . Starting from these observations, it is possible to conclude that the support plays an important role in the adsorption process, while the evolution of HCHO molecule (e.g. decomposition/reaction) is related to the metal phase, i.e. to the source of active oxygen. The difference in activity recorded among the catalysts (Fig. 8) is difficult to be rationalized since they do not depend on the acidity or basicity, neither on the redox property of supports. At the same time, there is not a clear correlation with the dispersion of platinum as reported in other studies [29,32]. It is instead observed an inverse dependence between HCHO conversion and the ratio between the exposed area of the metal and the surface area of support as reported in Fig. 9. Pt-exposed area has been calculated on the basis of the dispersion obtained from HRTEM images and by assuming spherical metal particles. This picture suggests that at room temperature, a key parameter is a high surface area of the support that positively affects the catalytic activity; thanks to its capability to adsorb formaldehyde. It is interesting to point out that Pt/ CeO_2 -N shows a lower activity compared to its ratio between metal area and surface area of the support, suggesting that in this material, the oxidation mechanism follows different routes. In particular, it can be hypothesized that ceria contributes to maintain Pt in a partially oxidized state despite the reduction treatment, and this condition lowers the catalytic activity towards HCHO oxidation. Another aspect that must be taken into account in the correlation between TPO and TPD and catalytic results is that the latter ones refer to a steady state outlet composition after 2 h of reaction where the reactants (HCHO, H_2O and O_2) have been fed simultaneously. It is possible that the continuous regeneration of hydroxyl group on the surface by providing water vapour constitutes an extra source of oxygen for the oxidation of formaldehyde. Recently, it was reported that Au/ Al_2O_3 catalysts show an outstanding activity at room temperature towards the oxidation of formaldehyde attributable to the presence of water vapour that guarantees hydroxyl groups on the surface of alumina. The OH groups, in turn, would favour the adsorption of HCHO and its oxidation [8,10]. Moreover, the presence of hydroxyl groups was also a key factor in promoting the water-gas shift reaction at low temperature over ZrO_2 -based catalysts [49]. In this perspective also, the support plays a prominent role in the catalytic oxidation of formaldehyde and it becomes important to evaluate the

different sources of activated oxygen. Among the supports considered in this work, CeO₂ is the more reducible and has an alternative route to provide oxygen that might explain its different behaviour (Fig. 9). In this case though, the extra oxygen is not directed to HCHO but to oxidize platinum that becomes less reactive towards formaldehyde decomposition. To summarize, under the operating conditions of this study, the activity of the investigated catalysts is related to the dynamic equilibrium established between reactants and products at the surface of catalyst that implies an active role of the support in adsorbing and oxidizing HCHO through the hydroxyl groups present on its surface.

5. Conclusions

This study investigated the activity of Pt-based catalysts on four different oxides (Al₂O₃, ZrO₂, TiO₂ and CeO₂) towards the oxidation of formaldehyde at room temperature. For Pt dispersion of about 40–60%, the results obtained evidence that the support plays a fundamental role in favouring the conversion of formaldehyde. Moreover, these results conclude that for the development of a promising catalyst, the support should satisfy the following key requirements: - good adsorption capacity and high surface area in order to maximize the concentration of active intermediates on the surface and to guarantee high accessibility to the metal active sites at the same time; - strong affinity for water in order to allow a high surface hydroxylation, which promotes the adsorption and oxidation of formaldehyde; - tuned redox properties that can favour Pt dispersion through an appropriate metal-support interaction, and at the same time avoid its partial oxidation.

Acknowledgements

The authors are grateful to Regione Friuli Venezia Giulia for financial support.

References [1] T. Salthammer, S. Mentese, R. Marutzky, *Chem. Rev.* 110 (2010) 2536. [2] W. Ye, J.C. Little, D. Won, X. Zhang, *Build. Environ.* 75 (2014) 58. [3] J.D. Schroeter, J. Campbell, J.S. Kimbell, R.B. Conolly, H.J. Clewell, M.E. Andersen, *Toxicol. Sci.* 138 (2014) 412. [4] D. Coggon, G. Ntani, E.C. Harris, K.T. Palmer, *Am. J. Epidemiol.* 179 (2014) 1301. [5] H. Guo, F. Murray, S.C. Lee, *Build. Environ.* 38 (2003) 1413. [6] C.J. Ma, X.H. Li, T.L. Zhu, *Carbon* 49 (2011) 2873. [7] E.M. Carter, L.E. Katz, G.E. Speitel, D. Ramirez, *Environ. Sci. Technol.* 45 (2011) 6498. [8] D. Chen, Z.P. Qu, Y.H. Sun, Y. Wang, *Colloid Surf. A* 441 (2014) 433. [9] J.Q. Torres, S. Royer, J.P. Bellat, J.M. Giraudon, J.F. Lamonier, *ChemSusChem* 6 (2013) 578. [10] B.B. Chen, X.B. Zhu, M. Crocker, Y. Wang, C. Shi, *Catal. Commun.* 42 (2013) 93. [11] B.B. Chen, X.B. Zhu, M. Crocker, Y. Wang, C. Shi, *Appl. Catal. B: Environ.* 154 (2014) 73. [12] H.B. Huang, D.Y.C. Leung, *ACS Catal.* 1 (2011) 348. [13] L.H. Nie, Y.Q. Zheng, J.G. Yu, *Dalton Trans.* 43 (2014) 12935. [14] R. Averlant, S. Royer, J.M. Giraudon, J.P. Bellat, I. Bezverkhyy, G. Weber, J.F. Lamonier, *ChemCatChem* 6 (2014) 152. [15] Z.P. Qu, Y.H. Sun, D. Chen, Y. Wang, *J. Mol. Catal. A: Chem.* 393 (2014) 182. [16] C.B. Zhang, Y.B. Li, Y.F. Wang, H. He, *Environ. Sci. Technol.* 48 (2014) 5816. [17] B.Y. Bai, J.H. Li, *ACS Catal.* 4 (2014) 2753. [18] Y. Chen, J.H. He, H. Tian, D.H. Wang, Q.W. Yang, *J. Colloid Interface Sci.* 428 (2014) 1. [19] C.B. Zhang, F.D. Liu, Y.P. Zhai, H. Ariga, N. Yi, Y.C. Liu, K. Asakura, M. Flytzani-Stephanopoulos, H. He, *Angew. Chem. Int. Ed.* 51 (2012) 9628. [20] B.C. Liu, C.Y. Li, Y.F. Zhang, Y. Liu, W.T. Hu, Q. Wang, L. Han, J. Zhang, *Appl. Catal. B: Environ.* 111 (2012) 467. [21] H.Y. Chen, Z.B. Rui, H.B. Ji, *Ind. Eng. Chem. Res.* 53 (2014) 7629. [22] L. Ma, D.S. Wang, J.H. Li, B.Y. Bai, L.X. Fu, Y.D. Li, *Appl. Catal. B: Environ.* 148 (2014) 36. [23] L.H. Nie, P. Zhou, J.G. Yu, M. Jaroniec, *J. Mol. Catal. A: Chem.* 390 (2014) 7. [24] Q.L. Xu, W.Y. Lei, X.Y. Li, X.Y. Qi, J.G. Yu, G. Liu, J.L. Wang, P.Y. Zhang, *Environ. Sci. Technol.* 48

(2014) 9702.[25] C.B. Zhang, H. He, K. Tanaka, *Catal. Commun.* 6 (2005) 211.[26] J.X. Peng, S.D. Wang, *J. Phys. Chem. C* 111 (2007) 9897.[27] L.F. Wang, M. Sakurai, H. Kameyama, *J. Hazard. Mater.* 167 (2009) 399.[28] H.B. Huang, D.Y.C. Leung, D.Q. Ye, *J. Mater. Chem.* 21 (2011) 9647.[29] H.B. Huang, P. Hu, H.L. Huang, J.D. Chen, X.G. Ye, D.Y.C. Leung, *Chem. Eng. J.* 252(2014) 320.[30] L.H. Nie, J.G. Yu, J.W. Fu, *ChemCatChem* 6 (2014) 1983.[31] N.H. An, P. Wu, S.Y. Li, M.J. Jia, W.X. Zhang, *Appl. Surf. Sci.* 285 (2013) 805.[32] J.X. Peng, S.D. Wang, *Appl. Catal. B: Environ.* 73 (2007) 282.[33] N.H. An, W.L. Zhang, X.L. Yuan, B. Pan, G. Liu, M.J. Jia, W.F. Yan, W.X. Zhang, *Chem. Eng. J.* 215 (2013) 1.[34] S. Imamura, Y. Uematsu, K. Utani, T. Ito, *Ind. Eng. Chem. Res.* 30 (1991) 18.[35] X.F. Tang, J.L. Chen, X.M. Huang, Y. Xu, W.J. Shen, *Appl. Catal. B: Environ.* 81(2008) 115.[36] R.H. Wang, J.H. Li, *Catal. Lett.* 131 (2009) 500.[37] H.B. Huang, D.Y.C. Leung, *J. Catal.* 280 (2011) 60.[38] H. Lieske, G. Lietz, H. Spindler, J. Völter, *J. Catal.* 81 (1983) 8.[39] A. Trovarelli, *Catal. Rev.* 38 (1996) 439.[40] D.H. Mei, N.A. Deskins, M. Dupuis, *Surf. Sci.* 601 (2007) 4993.[41] S.D. Senanayake, D.R. Mullins, *J. Phys. Chem. C* 112 (2008) 9744.[42] B.T. Teng, S.Y. Jiang, Z.X. Yang, M.F. Luo, Y.Z. Lan, *Surf. Sci.* 604 (2010) 68.[43] C. Ratnasamy, J.P. Wagner, *Catal. Rev.* 51 (2009) 325.[44] G.A. Attard, H.D. Ebert, R. Parsons, *Surf. Sci.* 240 (1990) 125.[45] L. Ke, pi ´nski, J. Okal, *J. Catal.* 192 (2000) 48.[46] J. Soria, A. Martinez-Arias, J.M. Coronado, J.C. Conesa, *Top. Catal.* 11 (2000) 205.[47] Y.B. Zhang, Y.N. Shen, X.Z. Yang, S.S. Sheng, T. Wang, M.F. Adebajo, H.Y. Zhu, *J. Mol. Catal. A: Chem.* 316 (2010) 100.[48] D.I. Kondarides, X.E. Verykios, *J. Catal.* 174 (1998) 52.[49] M. Vicario, J. Llorca, M. Boaro, C. de Leitenburg, A. Trovarelli, *J. Rare Earth* 27(2009) 196.