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Promotional effect of gold added to palladium supported on a new mesoporous TiO_2 for total oxidation of volatile organic compounds

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Abstract

Gold and palladium were supported on a mesoporous TiO_2 for total oxidation of volatile organic compounds (VOCs). Mesoporous high surface area titania support was synthesised using of $Ti(OC_2H_5)_2$ in the presence of CTMABr surfactant. After removing the surfactant molecules, 0.5 or 1.5 wt% of palladium and 1 wt% of gold were precipitated on the support by, respectively, wet impregnation and deposition–precipitation methods. The activity for toluene and propene total oxidation of the prereduced samples follows the same order: $0.5\%Pd\text{-}1\%Au/TiO_2 > 1.5\%Pd/TiO_2 > 0.5\%Pd/TiO_2 > 1\%Au\text{-}0.5\%Pd/TiO_2 > 1\%Au/TiO_2 > TiO_2$. Moreover, a catalytic comparison with samples based on a conventional TiO_2, shows the catalytic advantage of the mesoporous TiO_2 support. The promotional effect of gold added to palladium could be partly explained by small metallic particles (TEM), but meanly by metallic particles made up of Au-rich core with a Pd-rich shell. Moreover, the hydrogen TPR profile of $0.5\%Pd\text{-}1\%Au/TiO_2$ shows only the signal attributed to small PdO particles. Gold also implies a protecting effect of the support under reduction atmosphere. Operando diffuse reflectance infrared fourier transform (DRIFT) spectroscopy was carried on and allowed to follow the VOCs oxidation and the formation of coke molecules, but also a metallic electrodonor effect to the adsorbed molecule which increases in the same order as the activity for oxidation reaction. The presence of coke after test was also shown by DTA–TGA by exothermic signals between 300 and 500 °C and by EPR ($g = 2.003$).

Keywords: VOC oxidation; Palladium; Gold; Mesoporous titania

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1. Introduction

The development of active catalysts for total combustion of volatile organic compounds (VOCs) is desired from the viewpoint of environmental protection. Noble metals which possess high activity for total oxidation are widely applied to the low temperature complete oxidation [1,2]. Bimetallic catalysts have attracted extensive attention because of their markedly different properties from either of the constituent metals, and often enhanced catalytic stabilities, activities and/or selectivities [3]. Moreover, palladium catalysts are well known for high activity in oxidation reactions [4] and modification of palladium with gold can result in improvement of the catalytic activity of palladium. The addition of a second metal can favour the reduction of the first, increase the dispersion of a metal which has a tendency to form large particles or decrease its fritting [5]. Thus, Pd-Au metals based catalysts were found to be more active for several reactions as trichloroethene hydrodechloration [6], acetoxylation of ethylene [7] and direct synthesis of hydrogen peroxide from H_2 and O_2 [8] than Pd based catalysts.

Morever, it was found that the support plays an important role in the improvement of the efficiency of the catalyst, particularly in oxidation reaction. Various metal oxides, including TiO_2, have been investigated as gold and/or palladium supports, with the aim of high catalytic activity [9]. Moreover, TiO_2 was used to support Pd-Au leading to a good catalyst for H_2 oxidation to H_2O_2 [8] and TiO_2 was shown to have a unique chemistry in stabilizing Au particles and/or participating in the oxidation reaction [9]. Indeed, recently

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many nanostructured mesoporous oxides with high surface areas and uniform pore size distributions are used as support for multiple catalyst applications [10–12]. Thus, their high surface areas and porous volumes are real assets to improve plenty of catalytic reactions and adsorption/separation performance. For example, nanostructured mesoporous zirconia and titania supports for vanadia and gold catalysts have provided excellent catalytic properties for complete benzene oxidation [10] and the mesoporous TiO_2 used in this work, impregnated by Pd, was found to be a very active catalyst for VOC total oxidation [13].

In this work, we studied the promotional effect of gold added to palladium by the use of gold and/or palladium mono and bimetallic phase supported on mesoporous TiO_2 for total oxidation of volatile organic compounds.

Propene and toluene were used as probe molecule because alkenes and aromatics are present in the industrial and automotive emissions and they present important photochemical ozone creativity potential (POCP) [14]. As VOCs are precursor of ozone through a modification of the Chapman's cycle, a POCP scale relative to POCP of ethylene (=100) was established by Derwent et al. [14] allowing to attribute a value for each VOC.

2. Experimental

Mesoporous high surface area titania support was synthesised by the use of $Ti(OC_2H_5)_2$, as titanium oxide precursors in the presence of surfactant CTMABr [15] and was calcined at 400 °C under air. The solid was characterised by XRD, TEM, SEM and BET [13].

After removing the surfactant molecules, the new support is precipitated by 0.5 or 1.5 wt% of palladium and 1 wt% of gold. Gold was deposited using deposition–precipitation method [16]. The amount of TiO_2 required was dispersed into a solution containing $HAuCl_4$ heated to 80 °C. The pH of the solution was adjusted to 8 with NaOH. The suspension of TiO_2 in the solution was stirred for 4 h at 80 °C. After the deposition–precipitation, the sample was washed with water (60 °C) six times, and dried 24 h at 80 °C. Palladium supported samples were prepared by aqueous impregnated method using palladium nitrate and all the samples were calcined in air at 400 °C for 4 h. The solids obtained, 1%Au/TiO_2, 1%Au-0.5%Pd/TiO_2, 0.5%Pd-1%Au/TiO_2, 0.5%Pd/TiO_2 and 1.5%Pd/TiO_2, were all characterised by elementary analysis, thermal analysis, specific area analysis, X-ray diffraction and H_2 temperature programmed reduction (TPR), electron paramagnetic resonance (EPR) and transmission electron microscopy (TEM). Moreover, for a comparison purpose, samples prepared from palladium and gold supported on a conventional titania oxide (called 0.5%Pd/conventional TiO_2 and 0.5%Pd-1%Au/conventional TiO_2) were also synthesised by the same procedure. This support coming from Huntsman Tioxide (sulphate method) and calcined at 400 °C possesses a high specific surface of 134 $m^2\,g^{-1}$.

The palladium and gold content was determined by the Analytical Center of French CNRS (Vernaison) by inductive coupled plasma optical emission spectroscopy and mass spectroscopy (ICP/OES/MS) after dissolution of sample on a mixture of HF and HNO_3 solution.

Thermal analysis measurements were performed using a Netzsch STA 409 equipped with a microbalance differential analysis (DTA) and a flow gas system. The dried catalyst was treated under air; the temperature was raised at a rate of 5 °C min^{-1} from room temperature to 1000 °C.

N_2 adsorption–desorption isotherms and BET specific surface areas were measured at −196 °C with a volumetric adsorption analyser Sorptomatic 1990 manufactured by Thermo Finnigan.

The structures of solids were analyzed by powder X-ray diffraction (XRD) technique at room temperature with a Bruker diffractometer using Cu Kα radiation scanning 2θ angles ranging from 10° to 80°.

Temperature programmed reduction experiments were carried out in an Altamira AMI-200 apparatus. The TPR profiles were obtained by passing a 5% H_2/Ar flow (30 mL min^{-1}) through the calcined sample (about 100 mg). The temperature was increased from −40 to 500 °C at a rate of 5 °C min^{-1}. The hydrogen concentration in the effluent was continuously monitored by a thermoconductivity detector (TCD).

Electron paramagnetic resonance measurements were performed at −196 and 25 °C on an EMX Brüker spectrometer. A cavity operating with a frequency of 9.5 GHz (X band) was used. Precise g values were determined from simultaneous precise measuring of frequency and magnetic field values. All EPR spectra were treated with the Brüker WINEPR program.

TEM was performed on a Philips Tecnai-10 microscope at 100 kV. The specimens for TEM observation were prepared by embedding the samples in epoxy resin and ultramicrotoming and mounting on a copper grid.

The mono and bimetallic catalysts were tested in the oxidation of propene and toluene. Toluene and propene oxidation were carried out in a conventional fixed bed microreactor and studied between 25 and 400 °C (1 °C min^{-1}) 1) and with operando diffuse reflectance infrared fourier transform (DRIFT) spectroscopy. The reactive flow (100 N mL min^{-1}) was composed of air and 1000 ppm of gaseous toluene or propene. Before the catalytic test, the solid (100 mg) was calcined under a flow of air (2 L h^{-1}) at 400 °C (1 °C min^{-1}) and reduced under hydrogen flow (2 L h^{-1}) at 200 °C (1 °C min^{-1}).

3. Results and discussion

Elemental analysis of the samples was determined to especially verify the gold and palladium content. The results given in Table 1 are close to those expected.

XRD experiment of the calcined samples shows that the mesoporous TiO_2 support and the conventional TiO_2 present both the anatase phase with a low part of brookite phase for the mesoporous TiO_2 [13]. However, it was not possible to observe metallic gold and/or palladium or any of their oxides. The particle sizes are too small and/or there is not enough metal to observe these phases.

Table 1
Elemental analysis of the samples (gold and palladium content)

Sample	Metal (%)	
	Pd	Au
0.5%Pd/TiO_2	0.66	–
1%Au/TiO_2	–	0.96
0.5%Pd-1%Au/TiO_2	0.39	0.80
1%Au-0.5%Pd/TiO_2	0.37	0.79
1.5%Pd/TiO_2	1.27	–

The catalysts were tested for toluene and propene total oxidation. It is important to note that:

- whatever the catalyst used in toluene and propene total oxidation, CO_2 and H_2O are the only products formed without CO;
- the reduction step before test is important. For example, the T50 (temperature corresponding to a VOC conversion of 50%) for toluene oxidation on sample 0.5%Pd-1%Au/TiO_2 not reduced is 19 °C higher than the prereduced sample. Moreover, although the test has a reducing effect [17], the T50 of this sample reduced only during the test was still 10 °C higher than the prereduced sample;
- the mesoporous TiO_2 presents a better catalytic behaviour than the conventional TiO_2. Indeed the samples 0.5%Pd/conventional TiO_2 and 0.5%Pd-1%Au/conventional TiO_2 show higher T50, respectively, of 10 and 13 °C higher than those for the same samples based on mesoporous TiO_2.

Propene and toluene total oxidation curves versus temperature are presented, respectively, in Figs. 1 and 2. The activity for both propene and toluene oxidations, given by the T50 values (Table 2), follows the same order: 0.5%Pd-1%Au/TiO_2 > 1.5%Pd/TiO_2 > 0.5%Pd/TiO_2 > 1%Au-0.5%Pd/TiO_2 > 1%Au/TiO_2 > TiO_2.

Firstly, although the sample 1%Au/TiO_2 is more active than TiO_2, this catalyst is not very performing and the sample 0.5%Pd/TiO_2 is much better. Secondly, for the bimetallic sample, the catalyst 0.5%Pd-1%Au/TiO_2 shows the best activity whereas the sample 1%Au-0.5%Pd/TiO_2 is even less active than 0.5%Pd/TiO_2. Moreover, the sample 1.5%Pd/TiO_2, having the higher noble metal content, is less active than 0.5%Pd-1%Au/TiO_2. The impregnation of palladium on 1%Au/TiO_2 is therefore, very interesting for VOC oxidation and there must be a synergetic effect between Pd and Au on the catalyst obtained. Gold can electronically influence the catalytic properties of Pd [18]. Thus, Hutching and co-workers [19] had correlated the high activity for H_2 oxidation on Au-Pd/TiO_2 catalysts to a core-shell morphology with a gold-rich core and a palladium-rich surface. For these last two works Pd and Au are deposed together on the support before calcination. Although, our samples are prepared by successive metallic depositions, the best activity for 0.5%Pd-1%Au/TiO_2 can be explained by this morphology and the bad activity of 1%Au-0.5%Pd /TiO_2 by an inverse core-shell.

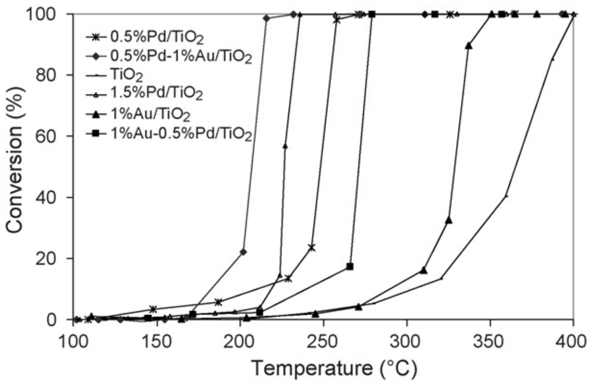

Fig. 1. Conversion of propene on different catalysts.

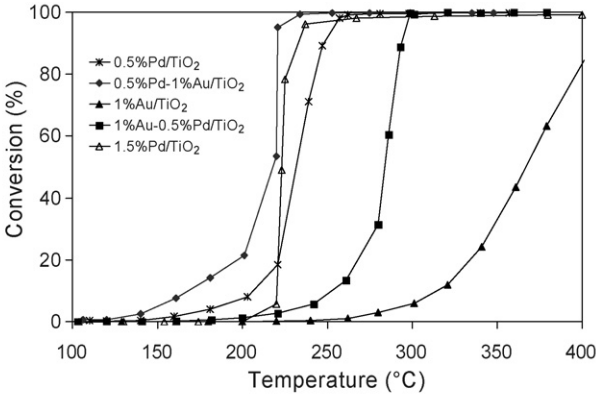

Fig. 2. Conversion of toluene on different catalysts.

The BET areas, the pore volume and the average pore diameter obtained by nitrogen adsorption–desorption isotherms (not shown) of the different samples were presented in Table 3. A small stepwise increase appears in the adsorption isotherms around $P/P_0 = 0.2$, indicating capillary condensation in the mesopores. BJH pore size curves obtained from the desorption branches of the isotherms indicate that the materials have well-defined mesopores. The pore volume and the average pore diameter values are close, respectively, to 0.46 $cm^3\,g^{-1}$ and 5.9 nm for all the samples. Loading the mesoporous titania with Pd and/or Au reduced its BET areas by about 15–40% from 200 $m^2\,g^{-1}$. As the BET area has not changed after impregnating the Au/TiO_2 by Pd, one can think that the Pd particles may be remaining on the Au particles, whereas BET areas after loading the Pd/TiO_2 by Au decreases. However, no

Table 2
T50 values for the samples

Sample	T_{50} (°C)	
	Propene	Toluene
TiO_2	367	–
0.5%Pd/TiO_2	250	230
1%Au/TiO_2	332	367
0.5%Pd-1%Au/TiO_2	208	219
1%Au-0.5%Pd/TiO_2	275	286
1.5%Pd/TiO_2	226	224

Table 3
BET surface areas before and after catalytic test (propene oxidation), pore volume and average pore diameter of the samples

Sample	BET surface area ($m^2 g^{-1}$)		Pore volume ($cm^3 g^{-1}$)	Pore diameter (nm)
	Calcined at 400 °C	After catalytic test		
TiO_2	200	174	–	–
0.5%Pd/TiO_2	173	154	0.489	5.88
1%Au/TiO_2	153	143	0.442	5.89
0.5%Pd-1%Au/TiO_2	151	127	0.460	5.89
1%Au-0.5%Pd/TiO_2	127	111	0.439	5.85
1.5%Pd/TiO_2	172	142	–	–

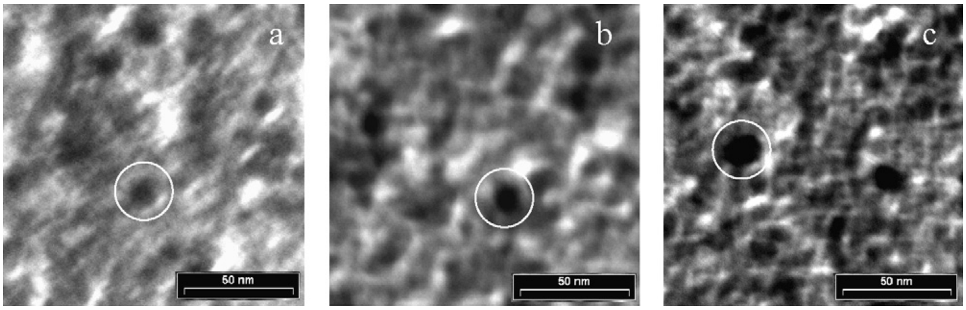

Fig. 3. Transmission electron microscopy pictures of: (a) 0.5%Pd/TiO_2, (b) 0.5%Pd-1%Au/TiO_2 and (c) 1%Au-0.5%Pd/TiO_2 with spots showing metallic particles.

direct relation was found between the BET areas and the catalytic activity of the catalysts.

The TEM pictures (Fig. 3) are not very clear, but allow to observe firstly, especially, in Fig. 3c, the presence of the disordered wormlike assembly of mesopores (white colour channels) and secondly the spherical metallic particles (black spots). For 0.5 wt% Pd/TiO_2, the smallest particles are observed with about 8–10 nm, but for the mixed metallic catalysts, the smaller ones are found on 0.5%Pd-1%Au/TiO_2 (10–12 nm) and not on 1%Au-0.5%Pd/TiO_2 (12–16 nm). Small metallic particles for 0.5%Pd-1%Au/TiO_2 could partly explain its high catalytic activity. However, the pictures are not enough fine to observe possible particles in the mesopores.

The TPR profiles of calcined catalysts are displayed in Fig. 4. The first signal of H_2 consumption at −20 °C observed for 1.5%Pd/TiO_2 (e) correspond to reduction of big PdO particles at the surface to Pd^0 [13].

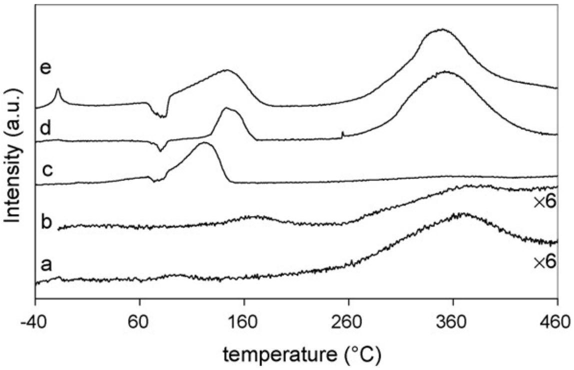

Fig. 4. H_2–TPR profile of calcined catalysts: (a) 1%Au-0.5%Pd/TiO_2, (b) 1%Au/TiO_2, (c) 0.5%Pd-1%Au/TiO_2, (d) 0.5%Pd/TiO_2 and (e) 1.5%Pd/TiO_2.

The negative peak at about 80 °C is due to the hydrogen desorption on palladium [20]. The third peak in the range 100–160 °C corresponds to the reduction of PdO particles more dispersed and/or in the porous structure. A low signal is also revealed for 1%Au/TiO_2 (b) due to oxygen on gold.

The large peak observed between 300 and 450 °C is due to the reduction of TiO_2. The presence of noble metal should enhance the reduction of TiO_2 [21,13]. However, the presence of gold leads to the decrease in the effect of palladium towards reduction and protects the TiO_2 support from reduction. The TPR profiles of (b) 1%Au/TiO_2 and (c) 0.5%Pd-1%Au/TiO_2 present only very low signals of TiO_2 reduction.

Moreover, it has been shown earlier that mesoporous titania was already more stable than classical TiO_2. X-ray diffraction patterns of mesoporous titania sample calcined at 400 °C shows the two phases anatase and brookite, whereas classical titania presents only anatase phase. This fact suggests that the presence of brookite could hinder the titania reduction and mesoporous titania reduction do not occur before 300 °C [13]. The catalytic activity could be correlated to the higher quantity and the lower reduction temperature of small PdO particles.

Operando DRIFT was carried on for propene and toluene reactions on samples 0.5%Pd-1%Au/TiO_2, 0.5%Pd/TiO_2 and 1%Au/TiO_2. For the propene reaction on 0.5%Pd-1%Au/TiO_2 catalyst (Fig. 5), the peak observed after introduction of propene at 1697 cm^{-1} (propene $\upsilon_{C=C}$) decreases since 150 °C and disappears after 250 °C as to propene conversion curve (Fig. 1) and broad bands between 1355 and 1854 cm^{-1} which should be generated from new compounds or cokes appear simultaneously.

Results of the same type were found for both the other catalysts for propene, but also for toluene oxidation according to their conversion curves. However, it was important to

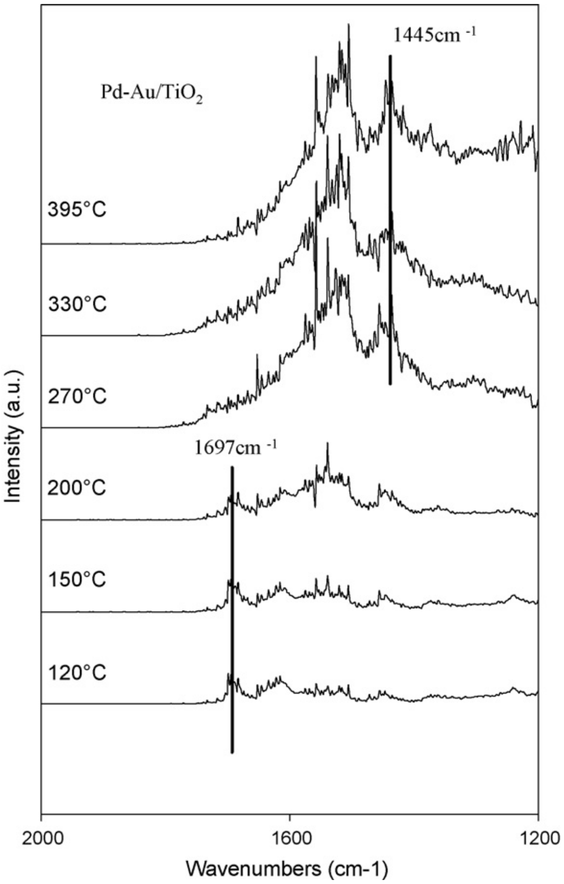

Fig. 5. Operando DRIFT spectra of propene on 0.5%Pd-1%Au/TiO_2.

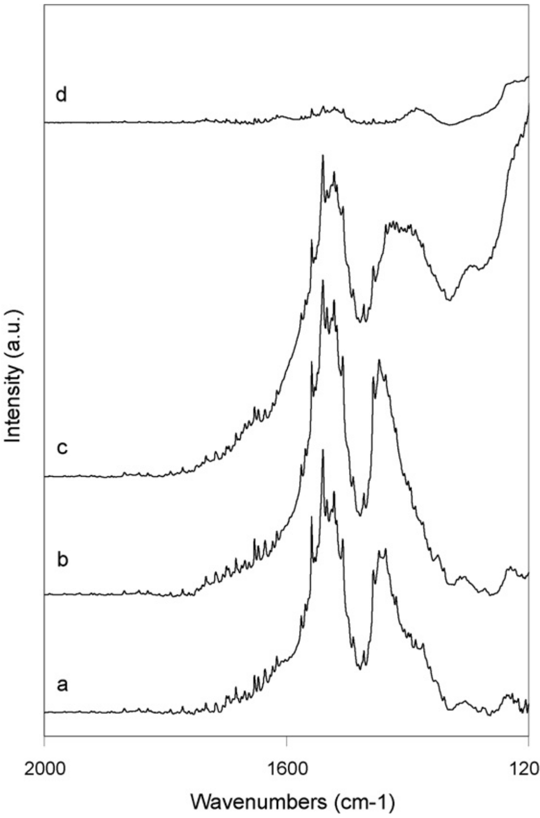

Fig. 6. Operando DRIFT spectra of combustion of coke (after propene oxidation) on 0.5%Pd-1%Au/TiO_2 in air: (a) before combustion, (b) 150 °C, (c) 300 °C and (d) 400 °C.

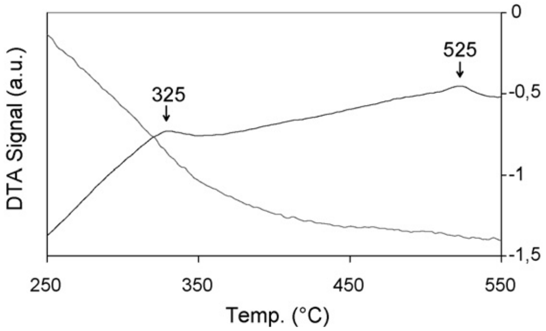

Fig. 7. DTA–TGA profile of 0.5%Pd-1%Au/TiO_2 (after the toluene catalytic test) under air.

observe that, the propene $\upsilon_{C=C}$ absorbance was shifted to lower wave number: 1693 cm^{-1} for 0.5%Pd/TiO_2 and 1670 cm^{-1} for 1%Au/TiO_2. The same band for isolated propene not adsorbed is at 1665 cm^{-1} [22]. Other bands corresponding to toluene adsorbed or coke can be studied and the same shift can be observed. The increase of the wave number of the $\upsilon_{C=C}$ band indicates a strengthening of the bond which can be due to a charge transfer from the catalyst to the adsorbed molecule. Indeed, some works on partial oxidation of propene on TiO_2 [23] show the existence of a charge transfer from TiO_2 to adsorbed molecules. Therefore, it seems that the catalyst presents a metallic electrodonor effect directly to the adsorbed molecule or via the TiO_2 support which increases in the same order than the activity for oxidation reaction.

The oxidation reaction of catalysts after catalytic test has been studied. The broads bands at 1531 and 1445 cm^{-1} corresponds to coke (aromatic C–C bonds) which is formed during propene or toluene oxidation (Fig. 6). Those bands of which intensities decrease between 300 and 400 °C, correspond to the combustion of coke and this is in agreement with the results obtained by DTA–TGA (Fig. 7) and by the EPR signal at *g* factor of 2.003 corresponding to coked catalyst (not shown) [24].

Thus, both the DTA exothermic signals at about 325 and 525 °C, observed for the studied samples after both the catalytic tests (Fig. 7 presents only the DTA–TGA profile of 0.5%Pd-1%Au/TiO_2 after the toluene catalytic test) should correspond to two types of hydrocarbon molecules, respectively, light coke corresponding to (polysubstituted) monoaromatic compounds and more heavy coke to polyaromatics [25]. Moreover, the specific surfaces of the samples after catalytic tests are found to be lower than before test. These measurements are supporting the DTA and EPR results concerning the coke deposit during the tests (Table 3).

4. Conclusion

Mesoporous high surface area titania support was synthesised by the use of $Ti(OC_2H_5)_2$ in the presence of CTMABr surfactant. After removing of surfactant molecules, about 0.5 or 1.5 wt% of palladium and 1 wt% of gold were precipitated on the support. The catalytic activity for toluene and propene total oxidation of the prereduced samples follows the same order: 0.5%Pd-1%Au/TiO_2 > 1.5%Pd/TiO_2 > 0.5%Pd/TiO_2 > 1%Au-0.5%Pd/TiO_2 > 1%Au/TiO_2 > TiO_2 and whatever the catalyst used, CO_2 and H_2O are the only products formed without CO. Moreover, a catalytic comparison with samples based on a conventional TiO_2 shows the catalytic advantage of the mesoporous TiO_2 support. The promotional effect of gold added to palladium observed for 0.5%Pd-1%Au/TiO_2 sample can be partly explained by the results of TEM, but especially by metallic particles made up of Au-rich core with a Pd-rich shell. For the mixed metallic catalysts, the smaller metallic particles are found on 0.5%Pd-1%Au/TiO_2 (10–12 nm). Moreover, the hydrogen TPR profile of 0.5%Pd-1%Au/TiO_2 shows only the signal attributed to small PdO particles and among all the studied catalysts, the reduction temperature of those particles is the lowest. In addition, gold implies also a protecting effect of the support towards reduction atmosphere. Actually palladium impregnated catalysts present a signal attributed to support reduction after 300 °C. When gold was first deposed on TiO_2, this signal was much lowered and slightly shifted to higher temperature. Otherwise, Operando DRIFT allowed following the VOCs oxidation, but also suggesting a metallic electrodonor effect to the adsorbed molecule which increases in the same order as the activity for oxidation reaction. Coke formation was observed too. The presence of coke after test was also shown by DTA–TGA by exothermic signals between 300 and 500 °C, by EPR with the signal at a factor $g = 2.003$ and a BET area decrease.

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