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Toluene deep oxidation over noble metals, Copper and Vanadium Oxides

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This work studies toluene abatement from gaseous streams, using gamma-Al_2O_3 supported palladium and platinum catalysts, titania and gamma-Al_2O_3 supported vanadium oxide catalysts and ZnO/Al_2O_3 supported copper oxide catalyst, characterized by textural and thermal analyses, X-ray diffraction and fluorescence. Noble metal catalysts have shown higher activity but lower selectivity toward total oxidation, with higher selectivity toward undesired products, like CO and benzene.

KEY WORDS: toluene; complete oxidation; palladium; platinum; vanadium; copper.

1. Introduction

Air quality has been a permanent concern of population and authorities. Although some countries have a good legislation about the subject, others have not or it is not applied properly, specially undeveloped ones. This way, some cities have a bad air quality and a lot of health problems registered, mainly respiratory sickness.

According to US Environmental Protection Agency – EPA, volatile organic compounds (VOCs) may be defined as any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions [1]. Some of which may have short and long-term adverse health effects. The main activities responsible for VOCs emissions are road transport, solvent utilization, storage/transport and industries [2]. Benzene, toluene and xylenes are among the most emitted VOCs.

Industries (especially petrochemical) are responsible for 9% of VOCs emissions in USA. This way, it is very important to control its emission levels. Several technologies are claimed to control VOCs emissions, like source control, collect systems, condensation, activated carbon adsorption, wet scrubbers, biological processes, criogeny, UV radiation, ozone, thermal incineration and combined methods [3], besides membrane processes [4]. Catalytic combustion seems to be a promising technology, which promotes high conversions in low temperature and residence time [5, 6].

Toluene is classified by US EPA as one of the most emitted VOCs in United States. Recent works report toluene deep oxidation over noble metals, specially platinum [7–13], palladium [9, 14] and rhodium [9, 15], besides copper [16] and chromium [17]. These catalysts generally show higher activity and selectivity toward complete oxidation, but they deactivate under the presence of halogens [7]. Oxide catalysts may be an alternative, with some advantages, like lower cost, higher chorine resistance [18] and the possibility to be used in other pollutant abatement reactions, like selective catalytic reduction (SCR) of NO_x, which is industrially performed over V_2O_5/TiO_2 catalysts [19, 20]. Toluene deep oxidation has been studied recently using uranium oxide [18], vanadium oxide [21, 22] and hydrotalcites [14], besides photocatalytic processes over titania [10, 23]. However, the number or works with these systems is much lower than the ones with noble metal catalysts.

The present work aims to compare the performance among noble metal catalysts (Pt/γ-Al_2O_3 and Pd/γ-Al_2O_3) and some oxides, like vanadium (V_2O_5/γ-Al_2O_3 and V_2O_5/TiO_2) and copper ($CuO/ZnO/Al_2O_3$), in toluene complete oxidation.

2. Experimental

2.1. Preparation

γ-Al_2O_3 (Al) and TiO_2 (Ti) (Degussa) and zinc/alumina mixed oxide (ZnAl) were used as supports in this

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study. Alumina was calcined at 500 °C for 2 h under flowing air while titania was only dried at 120 °C for 4 h before impregnation. Zinc/alumina mixed oxide (ZnAl) was prepared by co-precipitation of Zn^{2+} and Al^{3+} cations, using nitrate solutions as precursors and Na_2CO_3 0.3 M as precipitation solution, at 70 °C, aiming a ratio Zn:Al = 70:30. The suspension was stirred for 1 h and cooled under stirring for a further 1 h. The final pH was 7.8–8.0. After 50 min of decantation, the suspension was filtered and the solid washed with de-ionized water at 70 °C up to 0.2 ppm [Na^+], dried at 110 °C for 14 h and calcined at 350 °C for 4 h.

1 wt% Pt/γ-Al_2O_3 (1PtAl), 1 wt% Pd/$g\gamma$ -Al_2O_3 (1PdAl) and 1 wt% Cu/ZnO/Al_2O_3 (1CuZnAl) catalysts were prepared by incipient wetness impregnation of supports with aqueous solutions of hexachloroplatinic acid (H_2PtCl_6,Sigma), tetrachloride palladium acid (H_2PdCl_4, Sigma) and copper nitrate ($Cu(NO_3)_2.3H_2O$, Sigma), respectively, followed by drying at 120 °C for 16 h and calcination in air at 500 °C for 2 h (1PtAl and 1 PdAl) and 350 °C for 4 h (1CuZnAl).

1 wt% V_2O_5/γ-Al_2O_3 (1VAl) and 1 wt% V_2O_5/TiO_2 (1VTi) catalysts were prepared by wet impregnation of supports with aqueous solution of ammonium metavanadate (NH_4VO_3, Sigma). The solution was added to the support (30 cm^3/g), stirred in a rotavapor at room temperature and 120 rpm for 2 h, followed by a drying step under vacuum at 80 °C until complete elimination of solvent excess. Finally, the catalyst was dried at 120 °C for 16 h and calcined in air at 450 °C for 5 h.

2.2. Characterization

Chemical analyses of supports and catalysts were obtained by X-Ray Fluorescence. Samples were dissolved with fluoride, nitric or hydrochloric acids and analyzed on a RIX 3100 RIGAKU equipment. BET surface area was measured with a ASAP 2010 MICROMERITICS apparatus, using a high vacuum (10^{-5} Torr) system for degassing. After a drying step at 120 °C for one night, sample was cooled down to −196 °C and N_2 adsorption isotherms were collected, from $p/p_0 = 10^{-6}$ up to $p/p_0 = 1$. X-ray diffraction patterns of titania were recorded on a MINIFLEX RIGAKU spectrometer using Cu Kα (30 KV and 15 mA) radiation. Samples were not reduced for the analyses. Thermogravimetric (TGA) and differential thermal (DTA) analyses of titania were collected on a TAS 100 RIGAKU (with TG 8110 accessory), heating the sample from 25 to 800 °C (10 °C/min) under air flow, using α-Al_2O_3 as the reference sample.

2.3. Catalytic Test

Toluene deep oxidation reaction was carried out in a tubular fixed-bed micro reactor loaded with 100 mg of catalyst and in gas phase at atmospheric pressure and different temperatures. A thermocouple was placed on top of the catalyst bed to measure catalyst temperature. Before each catalytic test, catalysts were dried *in situ* with flowing nitrogen at 120 °C for 16 h and cooled to room temperature. A reduction step was performed with 1.5% H_2/Ar flow at a rate of 10 °C/min up to 500 °C for 30 min for 1PtAl and 1PdAl catalysts. For 1CuZnAl, 1VTi and 1Val catalysts, an oxidation step was performed with air flow at 400 °C for 16 h. After reduction or oxidation step, catalysts were cooled down to 150 °C. Reaction mixture was prepared by bubbling synthetic air (50 cm^3/min) through a saturator containing toluene at 25 °C, resulting in a 141 ppm toluene mixture and a space velocity (WHSV) of 4.2 h^{-1}. Reactants and products were analyzed by on-line gas chromatograph (VARIAN CP3800), equipped with flame ionization and thermal conductivity detectors and a Carbobond 50 m 0.53 mm capillary column. Activity data were acquired at different temperatures, ranging from 150 to 450 °C in steps of 50 °C. Injections were performed 5 min after temperature stabilization. After the injection, temperature was raised to the next temperature. Then, data collected refer to initial activity at that temperature. Diffusional and thermal effects were not verified at the conditions applied. Total toluene conversion (%), temperature of 50% conversion (T_{50}), selectivity toward benzene (%) and CO/CO_2 selectivity ratio were the variables analyzed.

3. Results and Discussion

3.1. Characterization

BET surface areas of some supports and catalysts are shown in Table 1. γ-Al_2O_3 has presented much higher surface area than titania. Surface area of γ-Al_2O_3 has decreased slightly when platinum and vanadium were impregnated, which may be attributed to the closure of some pores. On the other hand, the opposite behavior was observed when vanadium was impregnated in titania. This behavior may be explained by Ti-O bond breakage in the presence of vanadium. [24]. Ionic radius difference between V^{5+} (0.58 Å) and Ti^{4+} (0.68 Å) may lead to a crystallographic adjustment which promotes a surface area increase, specially for low vanadium loadings, which do not affect titania pore volume.

Table 2 presents chemical analyses of catalysts obtained by X-Ray Fluorescence. Real loadings were closer to nominal ones, except for 1VTi, which presented a lower real value. This difference was compensated in the mass of this catalyst used in the catalytic test.

X-Ray pattern of titania used as support is displayed in figure 1. It can be seen that anatase peaks are dominant compared to rutile ones. Vanadium peaks could not be detected, neither in titania nor in alumina, probably due to the low vanadium loading used (1 wt%) and the low crystallinity of vanadium phase on the catalyst obtained.

Table 1

BET surface area of supports and catalysts. Al: γ-Al_2O_3; Ti: TiO_2; 1PtAl: 1% Pt/Al_2O_3; 1VAl: 1% V_2O_5/Al_2O_3; 1VTi: 1% V_2O_5/TiO_2

Material	Al	Ti	1PtAl	1VAl	1VTi
S_{BET} (m^2/g)	223 ± 10	28.6 ± 1.6	199 ± 9	213 ± 10	40.9 ± 2.0

Thermogravimetric (TGA) and differential thermal (DTA) analyses of titania are shown in Figure 2. These spectra were not recorded for γ-Al_2O_3 because this material only shows phase transition above 1100 °C. Metallic ions addition may reduce transition temperature to 1000 °C [25]. Even in this case the temperature is much higher than the ones used in this work. It can be noted a mass loss above 150 °C, but an anatase-rutile phase transition, which generally occurs at 450 °C, cannot be observed, indicating a stability of this material up to this temperature.

3.2. Catalytic test

Catalysts have showed high stability under the conditions applied in this work, keeping the activity after 24 h of reaction. Selectivity toward complete oxidation was generally high (above 90%). Benzene was the only hydrocarbon found as by-product. Figure 3 reports the activity of supports and catalysts utilized and in gas phase. Gas phase reaction turnover is negligible compared to the one promoted by the catalysts, since conversion above 10% is only observed in gas phase at high temperatures (450 °C). Concerning the supports, γ-Al_2O_3 has shown a very low activity, slightly superior to the gas phase one, proving the inertness of this material. On the other hand, titania in anatase phase has shown a good catalytic activity, specially above 400 °C. Krishnamoorthy *et al.* [26] have also found that TiO_2 exhibited activity in o-dichlorobenzene oxidation, but the addition of vanadia significantly enhances the activity of the catalyst. Concerning the catalysts, vanadium and copper oxides have presented lower activity than noble metals. Titania supported vanadium catalyst was the most active among the oxide catalysts, but the activity of titania may be taken into account. Oxide catalysts have shown lower T_{50} than its supports, as was observed by other authors [26], showing the promoting effect of active phases. According to Nieto *et al.* [27], tetrahedral V^{5+} species are the main vanadium species in V-Mg-O and VO_x/Al_2O_3 catalysts, presented in isolated and polymeric forms. $V^{5+} \rightarrow V^{3+}$ transition was observed after a reduction step, with a peak temperature of 466 °C. Andreeva *et al.* [28] have found that polyvanadate structures predominantly exist on the V_2O_5/TiO_2 and V_2O_5/ZrO_2 catalysts structure in the presence of gold and proved a synergistic effect between nanosize gold and vanadium oxide species expressed as a significant decrease in the reaction temperature of complete benzene oxidation in the presence of oxygen or ozone. They found that the gold-containing samples on both studied supports provide a considerably lower temperature of $V^{5+} \rightarrow V^{3+}$ transition on TPR, from 500 °C to 200°C on V_2O_5/TiO_2support. Huuhtanen and Anderrsson [21] have observed by XPS characterization that vanadium was present at V^{5+} on all fresh V_2O_5/Nb_2O_5 samples. Then, according to the references discussed before, which shows that $V^{5+} \rightarrow V^{3+}$ transition occurs at temperatures above the maximum temperature used in this work (450 °C), and since reduction step was not applied in this case, it may expect that only V^{5+} species are present under reaction conditions.

Table 2

Chemical analyses of catalysts

Catalyst	%Pt	%Pd	%Cu	%V_2O_5
1PtAl	1.12	–	–	–
1PdAl	–	1.07	–	–
1CuZnAl	–	–	1.06	–
1VAl	–	–	–	0.995
1VTi	–	–	–	0.790

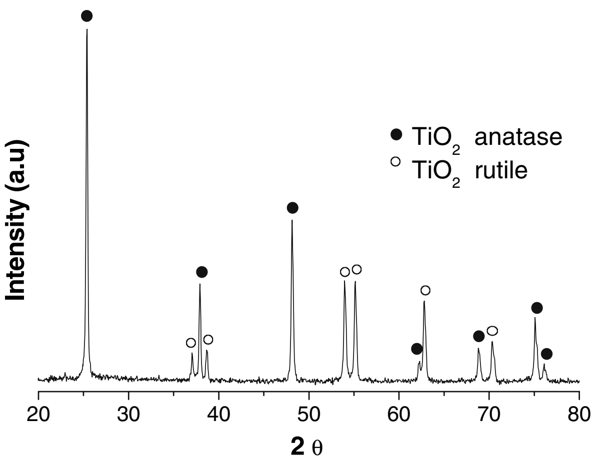

Figure 1. X-Ray Diffraction Pattern of titania used as support.

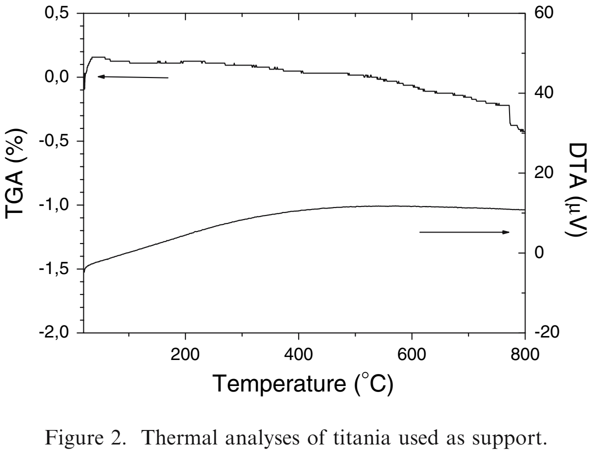

Figure 2. Thermal analyses of titania used as support.

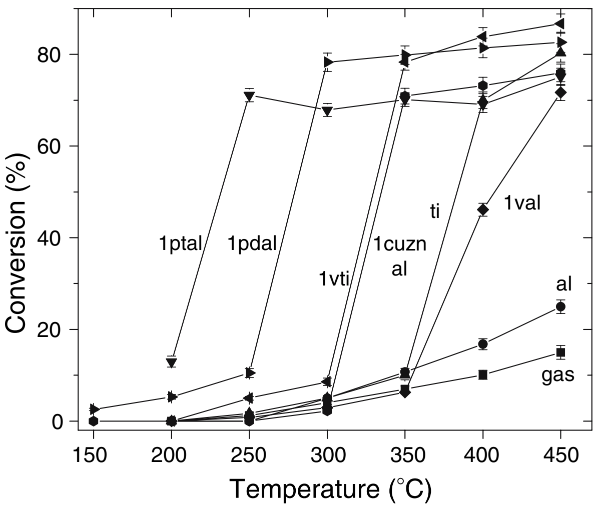

Figure 3. Activity of catalysts in toluene deep oxidation.

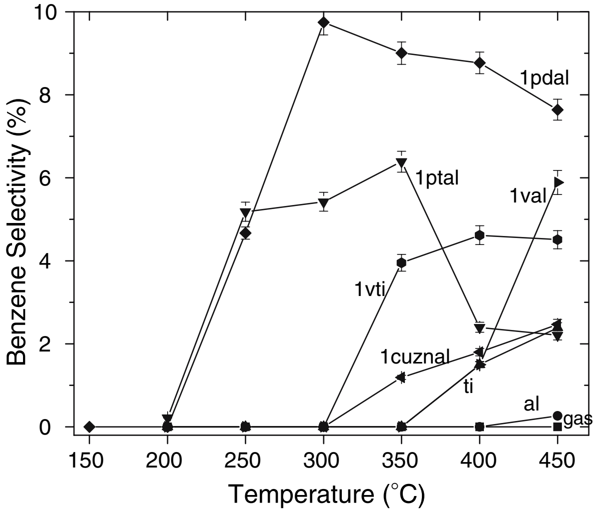

Figure 4. Benzene selectivity in toluene deep oxidation.

Platinum catalyst seems to be more active than palladium, having a T_{50} of 250 °C, while palladium showed a T_{50} of 300 °C. Patterson *et al.* [9] have obtained a similar result (higher activity of platinum) studying the oxidation of benzene, toluene and 1-hexene over alumina-supported noble metal catalysts. Paulis *et al.* [7] have found a T_{50} in the range of 197–239 °C for Pt/Al_2O_3 catalysts prepared from three different precursors. T_{50} found in this work for Pt/Al_2O_3 catalyst is slightly higher, but conversion was measured at each 50 °C. A smaller range of measure might be produced a closer result.

Concerning palladium catalyst, Ihm *et al.* [29] have found that hydrogen-treated 5 wt% Pd-γ-Al_2O_3 catalysts (mainly with metallic Pd) were more active for n-hexane complete oxidation at low-temperatures than air-treated catalysts (mainly with palladium oxide), even if the palladium oxide is known to be an active phase for high-temperature combustion of methane, and that the activity of reduced palladium catalysts decrease gradually during oxidation reaction and became equivalent to the activity of oxidized palladium catalysts. Since our catalyst was reduced before reaction, a similar behavior may be expected.

Selectivity toward benzene at several temperatures is shown in figure 4, while CO/CO_2 selectivity ratio is presented in figure 5. Deep oxidation is desirable by environmental point of view and can be represented by the following equation:

$$C_6H_5CH_3 + 9O_2 \rightarrow 7CO_2 + 4H_2O$$

Then, carbon monoxide and hydrocarbon (like methane and benzene) production indicates an incomplete oxidation. Methane could not be detected in the conditions applied in this work.

Since selectivity comparison has to be performed in isoconversion condition, data at 450 °C will be used in the following discussion, as all the experiments (except gas phase one) show similar conversion. Although noble metal catalysts have presented higher activity than oxides, they promote higher benzene selectivity, especially palladium. The selectivity toward benzene has a maximum at 300 °C for palladium and 350 °C for platinum. Oxide catalysts had increasing benzene selectivity with temperature.

Carbon monoxide production could not be detected with oxide catalysts, even at high temperature (450 °C). Noble metal catalysts showed an increasing CO/CO_2 selectivity ratio with temperature and palladium presented higher selectivity toward CO, undesirable by environmental point of view. Platinum seems to be more indicated for toluene complete oxidation than palladium, since it has showed higher activity and lower selectivity toward benzene and CO.

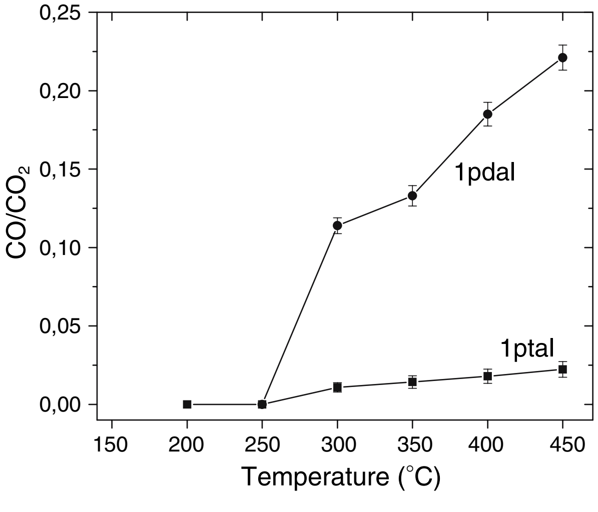

Figure 5. CO/CO_2 selectivity ratio of noble metal catalysts in toluene deep oxidation.

4. Conclusions

Toluene complete oxidation was studied over noble metals and oxide catalysts. Characterization of supports and catalysts has shown that titania used as support was in anathase phase stable under heating. Active phase impregnation has not changed specific surface area of supports significantly. Oxide catalysts show lower T_{50} than its supports, proving the promoting effect of active phases. Titania shows a reasonable activity for the reaction and it was concluded that V^{5+} species are responsible for the activity of vanadium catalysts. Noble metal catalysts, especially platinum, seem to be more active than oxides, with lower T_{50}. However, under isoconversion condition, they promote higher selectivity toward undesirable products by environmental point of view, like carbon monoxide and benzene, especially palladium catalyst. Selectivity toward benzene increase with temperature for oxides, while noble metal catalysts present a maximum around 300–350 °C. CO/CO_2 selectivity ratio always increases with temperature, but CO production could only be detected for noble metal catalysts.

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