Characterization and catalytic activity of Pd/V$_2$O$_5$/Al$_2$O$_3$ catalysts on benzene total oxidation

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Abstract

The role of vanadium oxide and palladium on the benzene oxidation reaction over Pd/V$_2$O$_5$/Al$_2$O$_3$ catalysts was investigated. The Pd/V$_2$O$_5$/Al$_2$O$_3$ catalysts were more active than V$_2$O$_5$/Al$_2$O$_3$ and Pd/Al$_2$O$_3$ catalysts. The increase of vanadium oxide content decreased the Pd dispersion and increased the benzene conversion. A strong Pd particle size effect on benzene oxidation reaction was observed. Although the catalysts containing high amount of V^{4+} species were more active, the Pd particle size effect was responsible for the higher activity.
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Keywords: Benzene oxidation; Pd/V$_2$O$_5$/Al$_2$O$_3$ catalysts; VOC removal

1. Introduction

Industrial waste gases from chemical and petrochemical plants contain different types of hazardous volatile organic compounds (VOCs) [1]. Several VOCs are toxic and can also contribute to the photochemical formation of various secondary pollutants in the atmosphere [2]. Therefore, more stringent environmental regulations have been developed and implemented in order to reduce the VOC emissions [3,4]. One of the techniques available for destructive removal of VOCs is catalytic oxidation [1,5,6].

Benzene is a VOC present in different industries, such as chemical, petrochemical, paint and coating industries and steel manufacture [7]. Several catalysts have been used for the total oxidation of benzene [8–16]. Base metal oxides, supported noble metals and combinations have been employed.

In general, supported noble metal catalysts are preferred due to their higher activity, since large gas volumes have to be treated, and their greater resistance to deactivation [5,17]. Papaefthimiou et al. [11] studied the catalytic oxidation of benzene on different group VIII metals supported on alumina. Pt and Pd were the most active catalysts. Recently, we studied the effect of the nature of support on

total benzene oxidation over Pd catalysts [18]. The catalytic activity depended on the nature of the palladium oxide species and thus on the strength of the Pd–O bond. The results strongly suggested that benzene oxidation mechanism should involve the Pd^0/Pd^{2+} pair. Lahousse et al. [10] compared the performances of MnO$_2$ (metal oxide) and Pt/TiO$_2$ on the total oxidation of different VOCs. Benzene was oxidized at lower temperatures over the Pt/TiO$_2$ catalyst.

However, metal oxides can be more active than noble metal catalyst in function of the nature of the VOC [10]. The oxidation of ethylacetate took place at lower temperature on MnO$_2$ than on the PtO$_2$ catalysts. Moreover, the metal oxide catalysts are more resistant to poisoning by compounds containing sulfur or chlorine [5].

Vassileva et al. [9] studied the benzene oxidation on 0.5% Pd/Al$_2$O$_3$, 30% V$_2$O$_5$/Al$_2$O$_3$ and 0.5% Pd/30% V$_2$O$_5$/Al$_2$O$_3$ catalysts. The 0.5% Pd/30% V$_2$O$_5$/Al$_2$O$_3$ catalyst presented higher conversions than the Pd/Al$_2$O$_3$ and V$_2$O$_5$/Al$_2$O$_3$ catalysts. These results were attributed to the modification of the vanadium oxidation state by the palladium addition. A redox mechanism was proposed to explain the catalytic behavior.

The aim of this work was to study the effect of palladium addition to V$_2$O$_5$/Al$_2$O$_3$ catalyst on the benzene total oxidation. The role of palladium and vanadium oxide species on benzene oxidation was proposed.

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2. Experimental

2.1. Catalyst preparation

γ-Al_2O_3 (Engelhard, AL-3916P) was calcined in air at 823 K for 16 h (BET area = 180 m^2/g). V_2O_5/Al_2O_3 samples were prepared by Al_2O_3 impregnation with an aqueous solution of ammonium methavanadate (Baker Analyzed) at room temperature during 1 h. The samples were dried at 353 K under vacuum and calcined under airflow at 773 K for 16 h. The Pd/Al_2O_3 and Pd/V_2O_5/Al_2O_3 samples were obtained by incipient wetness impregnation of Al_2O_3 and V_2O_5/Al_2O_3 samples with a solution of palladium chloride (Aldrich). Then, the samples were dried at 373 K, followed by calcination under airflow at 773 K for 2 h. The samples prepared and their metal contents determined by atomic absorption spectroscopy are given in Table 1.

2.2. X-ray diffraction (XRD)

XRD analysis were carried out in a Philips diffractometer PW 1410 using Cu Kα radiation (λ = 1.54050 Å) and Ni filter. The X-ray tube was operated at 40 kV and 30 mA and the X-ray pattern was scanned with a step size of 0.02° (2θ) from 10 to 80° (2θ) and counting time of 2.5 s per step.

2.3. Diffuse reflectance spectroscopy (DRS)

The UV-Vis diffuse reflectance spectra were recorded between 200 and 800 nm on a UV-Vis-NIR spectrometer (Cary 5-Varian) equipped with an integrating sphere (Harrick). In the case of Pd/Al_2O_3 samples, Al_2O_3 was used as reference. For Pd/x% V_2O_5/Al_2O_3 (x% = 5, 10 and 20 wt.%), the corresponding references of x% V_2O_5/Al_2O_3 samples were used.

2.4. Temperature programmed reduction (TPR)

TPR experiments were performed in a conventional apparatus, as described previously [19]. Before reduction, the catalysts were heated at 423 K in flowing nitrogen for 0.5 h. Then, a mixture of 4.7% hydrogen in nitrogen flow was passed through the sample and the temperature was raised from 298 up to 1173 K at a heating rate of 10 K/min.

2.5. Hydrogen chemisorption

H_2 uptakes were measured in an ASAP 2000C equipment (Micromeritics). Before the reduction, the catalysts were dried at 423 K for 0.5 h under vacuum. Then, the catalysts were reduced at 773 K (5 K/min) in flowing H_2 (30 cm^3/min). Following reduction, the samples were evacuated for 1 h at reduction temperature and cooled down to adsorption temperature under vacuum. Irreversible uptakes were determined from dual isotherms measured for hydrogen (at 343 K) using the method described by Benson et al. [20].

2.6. Benzene oxidation

The oxidation of benzene was performed in a tubular fixed bed reactor (Pyrex) at atmospheric pressure. The sample (60 mg) was reduced under hydrogen at 773 K for 1 h. After reduction, the reaction was carried out from 373 to 773 K in intervals of 20 K. The reaction mixture consisted of air/benzene (AGA; 482 ppm of benzene) at a flow rate of 30 ml/min (space velocity: 30,000 h^{-1}). Analyses of the products were carried out by on line gas chromatography (FID) with a column Porapak Q (6 m, carrier gas: H_2). A gas chromatograph equipped with a thermal conductivity detector and molecular sieve and Porapak QS columns were also used for CO and CO_2 analysis. It is important to stress that CO_2 and H_2O was the only product formed.

3. Results and discussion

3.1. The nature of vanadium oxide species on Pd/V_2O_5/Al_2O_3

The X-ray diffraction patterns of Al_2O_3 support and Pd/V_2O_5/Al_2O_3 sample are shown in Fig. 1. The diffraction patterns of 1 and 5% Pd/V_2O_5/Al_2O_3 sample displayed only the Bragg lines characteristics of Al_2O_3 phase. On the Pd/10% V_2O_5/Al_2O_3 sample, the lines corresponding to V_2O_5 were detected. The peaks characteristic of V_2O_5 were well defined on the Pd/20% V_2O_5/Al_2O_3 sample. These results are in agreement with the DRX analysis of the respective V_2O_5/Al_2O_3 sample [15]. Then, DRX analysis did not identify any modification of vanadium oxide structure in the presence of palladium.

3.2. The nature and dispersion of the palladium in the presence of vanadium oxide

The DRS spectra of Pd/Al_2O_3 and Pd/V_2O_5/Al_2O_3 samples containing different vanadium contents are presented in Fig. 2. The spectrum of the Pd/Al_2O_3 sample exhibited three bands at 243, 280 and 405 nm. The band around 243 nm is attributed to a charge transfer transition from oxygen of the support to the d orbital of Pd [21]. The bands at 280 and
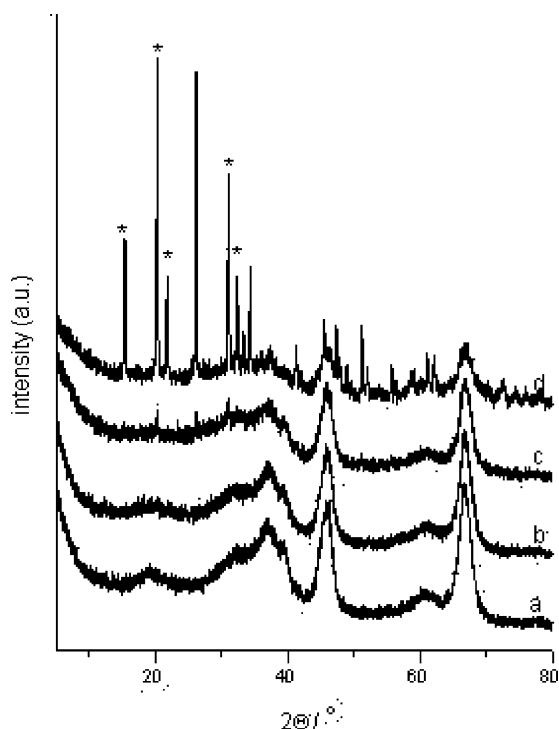
Table 1
Vanadium and palladium content for V_2O_5/Al_2O_3 and Pd/V_2O_5/Al_2O_3 samples

Catalysts	V (wt.%)	Pd (wt.%)
5% V_2O_5/Al_2O_3	4.0	–
10% V_2O_5/Al_2O_3	8.6	–
20% V_2O_5/Al_2O_3	20.4	–
Pd/Al_2O_3	–	0.81
Pd/5% V_2O_5/Al_2O_3	3.3	0.89
Pd/10% V_2O_5/Al_2O_3	8.8	0.80
Pd/20% V_2O_5/Al_2O_3	19.6	0.90

Fig. 1. X-ray diffraction patterns of: (a) Al_2O_3; (b) Pd/5% V_2O_5/Al_2O_3; (c) Pd/10% V_2O_5/Al_2O_3; (d) Pd/20% V_2O_5/Al_2O_3; (∗) position of the Bragg peaks for V_2O_5.

405 nm are due to metal–ligand charge transfer and d–d transition, respectively [22,23]. The DRS spectrum of Pd/5% V_2O_5/Al_2O_3 sample showed the band at 460 nm and a new one at 514 nm. On the Pd/10% V_2O_5/Al_2O_3 and Pd/20%
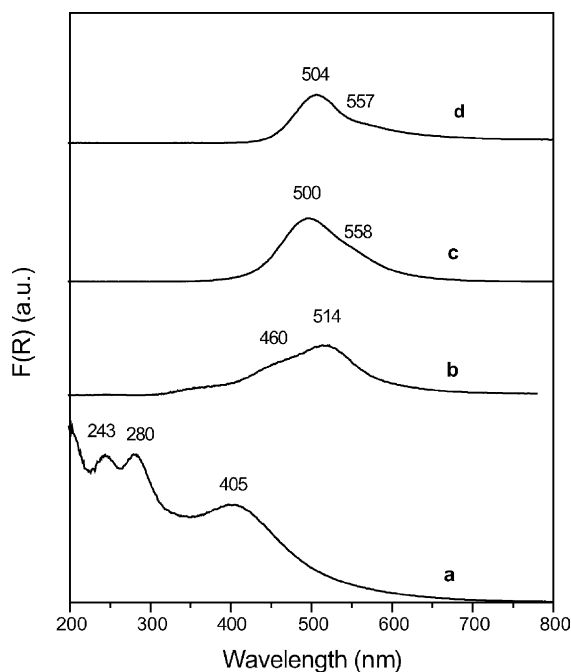

Fig. 2. DRS spectra of: (a) Pd/Al_2O_3; (b) Pd/5% V_2O_5/Al_2O_3; (c) Pd/10% V_2O_5/Al_2O_3; (d) Pd/20% V_2O_5/Al_2O_3.

V_2O_5/Al_2O_3 samples, it was observed the presence of a band and a shoulder at 500/558 and 504/557 nm, respectively.

The addition of vanadium modified significantly the spectra of the Pd/Al_2O_3 sample, leading to the disappearance of the band around 280 nm. The same result was observed in the literature for Pd/Al_2O_3 and Pd/SiO_2 catalysts calcined at different temperatures [18,22,24]. According to the authors, these results are due to the incorporation of oxygen into coordination sphere of Pd replacing chloride ions. Thus, the Pd^{2+} ions would be linked to surface oxygen atoms of the alumina support or would form small PdO particles. Noronha et al. [23] studied the effect of the addition of different Nb_2O_5 content on the Pd environment of Pd/Al_2O_3 sample through UV-Vis diffuse reflectance spectroscopy. Increasing the Nb_2O_5 content, the intensity of the charge transfer band around 287 nm decreased and this band was shifted towards higher wavelengths. This band was no more observed on the sample containing 20 wt.% of niobium oxide. The decrease of the intensity of the charge transfer band around 287 nm as the Nb_2O_5 loading increases suggested that less chloride ions were present on the Pd^{2+} coordination sphere.

Therefore, the addition of vanadium led to the complete removal of chloride ions from the coordination sphere of Pd in all Pd/V_2O_5/Al_2O_3 samples since the band at 280 nm disappeared. Furthermore, the bands around 450 and 550 nm correspond to d–d transition of PdO.

Table 2 shows the palladium dispersion calculated through H_2 chemisorption. The increase of vanadium oxide content strongly decreases the palladium dispersion. This result is in agreement with DRS analysis, which revealed the appearance of PdO particles in the presence of vanadium oxide. The PdO species is characteristic of catalysts with low Pd dispersion.

3.3. The effect of Pd addition on the reducibility of vanadium species

The presence of palladium also affected significantly the reduction of vanadium species. The TPR profile of Pd/V_2O_5/Al_2O_3 catalysts are presented in Fig. 3.

The Pd/Al_2O_3 catalyst exhibited one peak at 436 K (Fig. 3a). According to the literature [19,23,25–27], the peak around 436–465 K is attributed to the reduction of PdO_xCl_y species whereas the hydrogen consumption at low

Table 2

Palladium dispersion of the Pd/V_2O_5/Al_2O_3 catalysts calculated from the H_2 chemisorption measurements H_2, benzene reaction rates and turnover frequencies at 450 K of the palladium-based catalysts

Catalyst	D (%)	Reaction rate (g mol/g_{Pd} min) $\times 10^{-4}$	TOF (s^{-1}) $\times 10^{-4}$
Pd/Al_2O_3	40	0.20	0.9
Pd/5% V_2O_5/Al_2O_3	25	0.57	5.8
Pd/10% V_2O_5/Al_2O_3	18	1.32	13.1
Pd/20% V_2O_5/Al_2O_3	11	1.05	16.6

Reaction mixture: air/benzene (482 ppm of benzene).
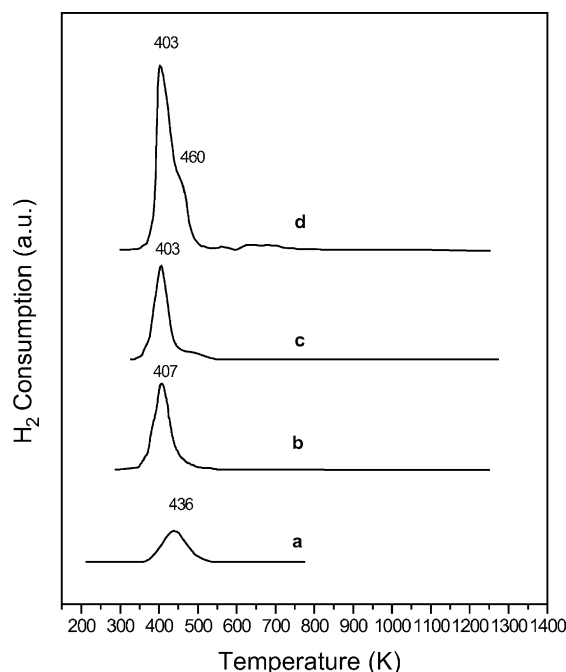
Fig. 3. TPR profiles of the Pd/V_2O_5/Al_2O_3 samples: (a) Pd/Al_2O_3; (b) Pd/5% V_2O_5/Al_2O_3; (c) Pd/10% V_2O_5/Al_2O_3; (d) Pd/20% V_2O_5/Al_2O_3.

Table 3
H$_2$ consumption and reduction degree of vanadium oxide obtained from the TPR analysis of the Pd/V_2O_5/Al_2O_3 samples

Catalyst	H$_2$ consumption (μmoles H$_2$/g$_{cat}$)	Reduction degree (%)[a]	Reduction degree (%)[b]
Pd/Al_2O_3	64	–	–
Pd/5% V_2O_5/Al_2O_3	568	183	92
Pd/10% V_2O_5/Al_2O_3	1328	154	77
Pd/20% V_2O_5/Al_2O_3	2701	137	68

The reduction degree of vanadium oxide was calculated from the total hydrogen uptake taking into account the hydrogen consumption due to palladium oxide.

[a] Reduction degree calculated considering the following reaction: $V_2O_5 + H_2 \rightarrow V_2O_4 + H_2O$.

[b] Reduction degree calculated considering the following reaction: $V_2O_5 + 2H_2 \rightarrow V_2O_3 + 2H_2O$.

temperature is due to PdO reduction. Frusteri et al. [27] investigated the influence of the Pd precursor on the nature of Pd oxides species. The Pd/Al_2O_3 catalysts were prepared using two different precursors: PdCl$_2$ and Pd(NH$_3$)$_4$(NO$_3$)$_2$. TPR analysis revealed two distinct peaks, which were correlated to the reduction of different PdO species. The TPR profile of Pd/Al_2O_3 chlorine-free catalyst exhibited one peak at low temperature (333 K) due to the reduction of PdO particles. The TPR analysis of the Pd/Al_2O_3 prepared from the PdCl$_2$ precursor displayed one peak at 393 K, which was assigned to the reduction of Cl-containing Pd^{2+} oxo-complexes strongly interacting with the alumina.

On the Pd/V_2O_5/Al_2O_3 catalysts, it is noted a peak around 400 K and a shoulder at 460 K on the catalysts containing a high vanadium loading. In accordance to the literature, the low-temperature peak could be attributed to the reduction of PdO particles over vanadium oxide. However, the hydrogen consumption at low-temperature reduction peak was significantly higher than the amount corresponding to the complete palladium oxide reduction (Table 3). This result suggested that vanadium oxide reduction also take place at this temperature range. In fact, it is no more observed a hydrogen uptake at high temperature, typical of the reduction of V_2O_5/Al_2O_3 samples [15]. Recently, we reported the characterization results of V_2O_5/Al_2O_3 samples by using TPR [15]. The reduction profile of 5% V_2O_5/Al_2O_3 catalyst showed a peak around 791 K. The TPR profile of 10% V_2O_5/Al_2O_3 catalyst exhibited a peak at 819 K while the 20% V_2O_5/Al_2O_3 catalyst displayed a peak around 869 K. Therefore, the addition of palladium strongly promoted the reduction of vanadium oxide at lower temperature.

Dancheva et al. [28] studied 30% V_2O_5/Al_2O_3 and Pd/30% V_2O_5/Al_2O_3 catalysts by TPR. The TPR profile of 30% V_2O_5/Al_2O_3 exhibited a peak at 803 K, whereas the Pd/30% V_2O_5/Al_2O_3 catalyst showed a peak at lower temperature (413 K). TPR analyses of Pd/Nb_2O_5/Al_2O_3 [23], Pd/CeO_2/Al_2O_3 [29] and Pd/MoO_3/Al_2O_3 [30] systems also revealed a strong promoting effect of palladium on the metal oxide reduction. According to the authors, hydrogen is activated on metallic palladium through dissociative adsorption to atomic hydrogen, which promotes the reduction of metal oxide. Therefore, our results agree very well with the literature and show the presence of a strong interaction between palladium and vanadium oxide on these catalysts.

The hydrogen consumption and the reduction degree during the TPR are presented in Table 3. After TPR, the average oxidation state of Pd/V_2O_5/Al_2O_3 catalysts was a function of vanadium oxide content. On the catalysts containing 5 wt.% of vanadium, the vanadium was mainly on the 3+ state whereas on the Pd/10% V_2O_5/Al_2O_3 and Pd/20% V_2O_5/Al_2O_3 there was a mixture of V^{4+} and V^{3+} ions.

3.4. The role of vanadium oxide and palladium on benzene oxidation

Fig. 4 exhibited the curves of benzene conversion as a function of reaction temperature on Pd/V_2O_5/Al_2O_3 catalysts. The catalysts containing a higher vanadium oxide content (Pd/10% V_2O_5/Al_2O_3 and Pd/20% V_2O_5/Al_2O_3) showed higher conversion of benzene. Table 2 presented the reaction rates of the benzene oxidation at 450 K. At this temperature, the conversion was lower than 10% and allows a comparison with catalytic data of the literature [11]. Increasing the vanadium content led to an increase of reaction rate. It is important to stress that the activity of V_2O_5/Al_2O_3 catalysts was negligible at this temperature [15].

The turnover frequency (TOF) of Pd/V_2O_5/Al_2O_3 catalysts on the benzene oxidation was calculated through both dispersion and reaction rates obtained by using conversion data taken at 450 K from the light off curves shown in Fig. 4. It is important to stress that the activity of V_2O_5/Al_2O_3
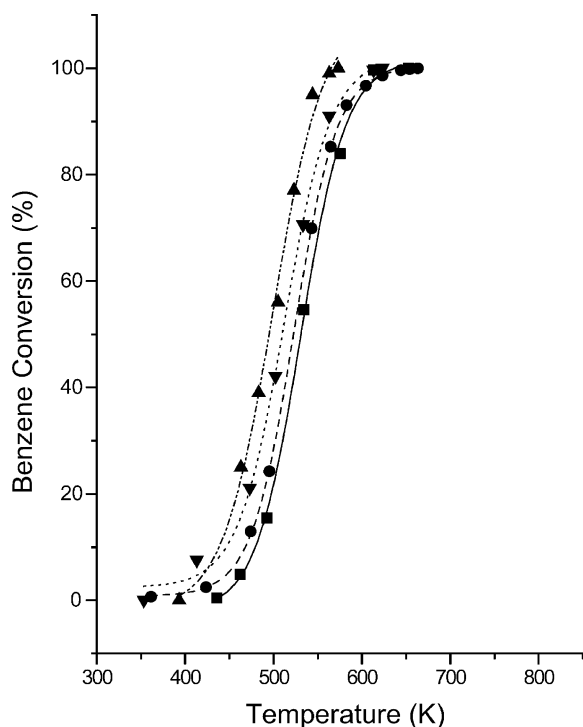
Fig. 4. Benzene conversion as a function of reaction temperature: (■) Pd/Al₂O₃; (●) Pd/5% V₂O₅/Al₂O₃; (▲) Pd/10% V₂O₅/Al₂O₃; (▼) Pd/20% V₂O₅/Al₂O₃.

Fig. 5. Turnover frequency at 450 K of the total benzene oxidation over catalysts of this work: (■) Pd/Al_2O_3; (●) $Pd/5\%$ V_2O_5/Al_2O_3; (▲) $Pd/10\%$ V_2O_5/Al_2O_3; (▼) $Pd/20\%$ V_2O_5/Al_2O_3. Catalysts from Ref. [18]: (○) Pd/Al_2O_3 calcined at 873 K; (△) Pd/Al_2O_3 calcined at 1073 K. Reaction mixture: air/benzene (482 ppm of benzene).

catalysts was practically null between 300 and 500 K [15] (Table 2). The TOF values of $Pd/V_2O_5/Al_2O_3$ catalysts presented the same order of magnitude of the ones observed in the literature on Pd/Al_2O_3 catalysts ($(1–2) \times 10^{-3} s^{-1}$) [11]. The increase of dispersion strongly decreased the TOF (Fig. 5), which suggested the presence of a particle size effect on the benzene oxidation reaction.

There is a controversy about the effect of the particle size on the catalytic hydrocarbon oxidation. Several authors have not observed a correlation between the particle size and TOF [31–34]. On the other hand, some works have shown a strong dependence between the activity and the particle size [35–40].

Papaefthimiou et al. [11] studied the effect of metal dispersion on the intrinsic activity of benzene oxidation on Pt/Al_2O_3 and Pd/Al_2O_3 catalysts. In the case of Pt/Al_2O_3 catalysts, the TOF of benzene oxidation enhanced significantly as the particle size increased. These results were attributed to the presence of chloride ions on the catalyst surface inhibiting the activity of Pt/Al_2O_3 catalysts. This inhibiting effect was more important on the highly dispersed catalysts. Otherwise, the TOF of benzene oxidation was independent of dispersion on Pd/Al_2O_3 catalysts.

Garetto and Apesteguía [16] studied the structure sensitivity of benzene combustion on Pt/Al_2O_3 catalysts. The benzene oxidation turnover rates were promoted on large Pt particles. According to the authors, the increase of Pt particle size increased the density of reactive Pt–O species, i.e., the number of Pt–O bonds of lower binding energy.
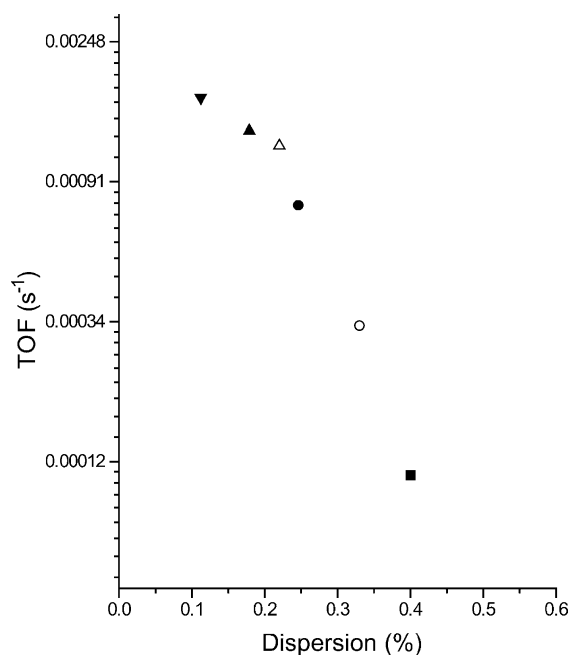
Pinto et al. [18] observed an increase of TOF of benzene oxidation reaction as the dispersion of Pd/Al_2O_3 catalysts calcined at different temperatures decreased. This particle size effect was associated to the nature of palladium oxide species and the strength of Pt–O band.

Generally, two types of PdO species are identified: bulk PdO and palladium oxide interacting with the support. The bulk PdO is characteristic of catalysts with low Pd dispersion. The second Pd specie is found on catalysts with high metal dispersion. Each of these Pd species has a different oxygen adsorption/desorption behavior. It has been observed that the strength of the Pd–O bond depends on the crystallite size [40–43]. The Pd–O bond strength increases as the particle size decreases.

Pinto et al. [18] identified the presence of two different states of Pd by XPS experiments. Pd/Al_2O_3 catalysts calcined at high temperature exhibited one peak at Pd $3d_{5/2}$ BE of 336.0 eV, which is characteristic of bulk PdO. These catalysts were reduced to metallic palladium at room temperature under hydrogen. On the samples calcined at low temperature, a peak and a shoulder were observed with Pd $3d_{5/2}$ BE at 336.1 and 337.0 eV. The high BE was attributed to the existence of small palladium clusters in interaction with the alumina support, which agrees well with the literature [42]. Widjaja et al. [43] observed the same results on Pd catalysts supported on Al_2O_3-based mixed oxides with different particle sizes. The core level BE of palladium (Pd $3d_{5/2}$) increased with decreasing crystallite size. The higher BE values are consistent with an increase in the Pd–O bond

strength as the Pd particle size decreases [39]. Therefore, Pinto et al. [18] attributed the variation of the TOF of the benzene total oxidation as a function of the Pd dispersion to changes on the electronic structure with the particle size.

It has been reported in the literature that the presence of chlorine has a poisoning effect on the activity of supported metallic catalysts on the oxidation of hydrocarbons. Therefore, the higher activity of $Pd/V_2O_5/Al_2O_3$ catalysts could be attributed to the absence of chlorine ions on these catalysts. However, in our work, the inhibiting effect of chlorine ions on the benzene oxidation can be rule out since the DRS results demonstrated that on alumina impregnated by vanadium oxide this ions were not present. Therefore, the benzene oxidation on $Pd/V_2O_5/Al_2O_3$ catalysts is a structure sensitive reaction.

However, it is important to determine the role of vanadium oxide on the $Pd/V_2O_5/Al_2O_3$ catalysts on the benzene oxidation.

Recently, we studied the performance of V_2O_5/Al_2O_3 catalysts on the benzene oxidation [15]. The following order of activity was observed: 20% V_2O_5/Al_2O_3 > 10% V_2O_5/Al_2O_3 > 5% V_2O_5/Al_2O_3. The reaction rates increased as the vanadium content increased. From DRS results after reaction, it was noted the presence of V^{4+} species on the 20% V_2O_5/Al_2O_3 catalyst, which exhibited the higher benzene activity. On the other hand, the 5% V_2O_5/Al_2O_3 catalyst did not show the band characteristic of V^{4+} species. Therefore, the higher activity to the total benzene oxidation on the catalyst containing high vanadium content was attributed to the high amount of V^{4+} species.

In order to analyze the role of vanadium oxide on $Pd/V_2O_5/Al_2O_3$ catalyst activity, the influence of the particle size have to be isolated. Therefore, the benzene conversions of Pd-V_2O_5 and Pd-only catalyst with the same particle size were compared. The data of two Pd/Al_2O_3 catalyst were obtained from Ref. [18]. The dispersion and the benzene conversion on Pd/Al_2O_3, $Pd/V_2O_5/Al_2O_3$ and V_2O_5/Al_2O_3 catalysts are listed in Table 4. A comparison between the activity of Pd/Al_2O_3 and $Pd/V_2O_5/Al_2O_3$ catalysts with the same dispersion shows that the benzene conversion on $Pd/V_2O_5/Al_2O_3$ catalysts corresponds approximately to the sum of benzene conversion on Pd/Al_2O_3 and V_2O_5/Al_2O_3 catalysts. These results suggests that there is no synergetic effect on the catalytic performance

of $Pd/V_2O_5/Al_2O_3$ catalysts on the benzene oxidation. On the other hand, if we compare the conversions of Pd/Al_2O_3 ($D = 22\%$) and Pd/10% V_2O_5/Al_2O_3 catalyst ($D = 18\%$), we can be induced to misleading conclusions. Actually, this result is mainly due to the lower dispersion of Pd/10% V_2O_5/Al_2O_3 catalyst. Then, the effect of Pd particle size outperforms the influence of the higher amount of V^{4+} species on the $Pd/V_2O_5/Al_2O_3$ catalysts containing 10 and 20 wt.% of vanadium.

Vassileva et al. [9] reported a promoting effect of Pd addition to a 30% V_2O_5/Al_2O_3 catalyst. The results were attributed to a modification of oxidation state of vanadium atoms by the palladium. The authors proposed a redox mechanism to explain the catalytic behavior. This mechanism involves the following steps: (i) oxidation of V^{4+} to V^{5+} and Pd^0 to Pd^{2+} by the oxygen; (ii) reduction of V^{5+} to V^{4+} and Pd^{2+} to Pd^0 by the hydrocarbon. The ion V^{3+} is relatively stable and should hardly participate of the reaction. However, the palladium dispersion of Pd/Al_2O_3 and $Pd/V_2O_5/Al_2O_3$ catalysts and the reaction rates are not supplied by the authors. Thus, a comparison between catalyst activity is not possible due to the strong influence of particle size effect on benzene total oxidation as previously described. It means that the redox mechanism proposed is probably taking place but it is not the main reason for the better catalytic behavior observed on the $Pd/V_2O_5/Al_2O_3$ catalyst.

4. Conclusions

The $Pd/V_2O_5/Al_2O_3$ catalysts were more active than V_2O_5/Al_2O_3 and Pd/Al_2O_3 catalysts. The $Pd/V_2O_5/Al_2O_3$ catalysts containing a higher vanadium oxide content presented lower dispersion and higher activity on the benzene oxidation reaction. The TOF of $Pd/V_2O_5/Al_2O_3$ catalysts increased as the dispersion decreased suggesting that the benzene oxidation on $Pd/V_2O_5/Al_2O_3$ catalysts is a structure sensitive reaction. In spite of the higher amount of V^{4+} species on the $Pd/V_2O_5/Al_2O_3$ catalysts containing 10 and 20 wt.% of vanadium, the effect of palladium particle size plays a role much more important on the benzene combustion.

Table 4
Benzene conversion at 525 K of the V_2O_5/Al_2O_3, $Pd/V_2O_5/Al_2O_3$ Pd/Al_2O_3 (from Ref. [18]) catalysts

Catalyst	Dispersion (%)	Benzene conversion (%)
Pd/Al_2O_3	22	43
5% V_2O_5/Al_2O_3	–	6
Pd/5% V_2O_5/Al_2O_3	25	56
Pd/Al_2O_3	17	61
10% V_2O_5/Al_2O_3	–	12
Pd/10% V_2O_5/Al_2O_3	18	80

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