

## TPSR, TPR, AND TPO STUDIES OF Pd-V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> CATALYSTS IN COMPLETE CATALYTIC OXIDATION OF BENZENE

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Alumina-supported palladium–vanadium pentoxide catalysts were studied by means of temperature-programmed surface reaction, temperature-programmed reduction, temperature-programmed oxidation, and by ESR spectroscopy in the complete oxidation of benzene. The surface reaction measurements indicated that 0.5% Pd–30% V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> produced most oxidation products, compared to 0.5% Pd/Al<sub>2</sub>O<sub>3</sub> or 30% V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> samples. A drastic fall of peak maxima in temperature-programmed oxidation and reduction spectra indicates the decisive role of palladium in the mixed metal–metal oxide system in facilitating the vanadium redox transitions. During initial period of catalysts operation, there proceeds formation of vanadium oxide phases which contain clustered V<sup>4+</sup> ions in a matrix of vanadium pentoxide. These ions are responsible for the high activity of the palladium–vanadium pentoxide catalyst.

In previous studies from this laboratory<sup>1,2</sup>, we reported on the high activity of the alumina-supported palladium–vanadium pentoxide catalyst in the complete oxidation of benzene with air oxygen. In the course of the reaction, depending upon experimental conditions, there proceeds formation of a catalytically active phase. Evidence for the promoting effect of palladium which facilitates transitions between various vanadium oxidation states was also presented.

The aim of this work was to provide an additional information concerning formation of the active phase and to obtain data on the synergic effect between catalyst components. The following techniques, particularly suitable for this purpose, were chosen: temperature-programmed surface reaction (TPSR), temperature-programmed reduction (TPR), temperature-programmed oxidation (TPO), and electron spin resonance (ESR) spectroscopy.

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## EXPERIMENTAL

### Sample Preparation and Treatment

The following samples were studied:  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Kobanyai Porcelangyar, BET area ca 150 m<sup>2</sup> g<sup>-1</sup>), 0.5 wt.% Pd/Al<sub>2</sub>O<sub>3</sub>, 30 wt.% V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub>, and 0.5 wt.% Pd-30 wt.% V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub>. These samples are further denoted as AlO, PdAlO, VAlO, and PdVAlO, respectively. For details on catalyst preparation see refs<sup>1,2</sup>. Samples of 40 – 80 mesh were used in the experiments. All the temperature-programmed studies were made with the use of an apparatus described elsewhere<sup>3</sup>. Each sample was pretreated by heating at 573 K for 3 h in a flow of air, followed by heating in helium flow (50 ml min<sup>-1</sup>) from room temperature up to 623 K at the rate 25 K min<sup>-1</sup>, to remove hydroxyl groups and chemisorbed oxygen from the sample surface.

### Temperature-Programmed Surface Reaction (TPSR)

The measurements were made with 0.2 g samples which were heated at a rate of 25 K min<sup>-1</sup>. A specially purified helium<sup>3</sup> (50 ml min<sup>-1</sup>) was applied as a carrier gas. The catalyst surface was saturated by three pulses of benzene at 523 K. Blank experiments showed that generally the saturation was attained during the third pulse. After interaction with the surface, the composition of each pulse was determined by gas chromatography. Gas chromatographic analysis was also made of the thermally desorbed species. For this purpose, a cool trap was connected to the apparatus just after the thermal conductivity detector. Thus pulses that passed over the catalyst as well as species desorbed during thermal reaction could be frozen and analyzed after thawing. Analyses were made on a Perkin-Elmer F-17 instrument equipped with a flame ionization detector or a thermal conductivity detector, using a 2 m column packed with 10 wt.% PEG 20M/Chromosorb W HP DMCS (80 – 100 mesh) or Porapak Q (100 – 120 mesh) and argon as a carrier gas at 30 ml min<sup>-1</sup> or 50 ml min<sup>-1</sup> flow rate. The rate of sample heating was 20 K min<sup>-1</sup> for the 373 – 443 K range and the injection part temperature was 423 K.

### Temperature-Programmed Reduction (TPR)

An argon-hydrogen mixture (13% H<sub>2</sub>) dried by passing through 0.5 nm-molecular sieve trap placed in a cool bath (223 – 233 K) was used (flow rate 24 ml min<sup>-1</sup>). The sample (0.06 g) was heated at rate 15 K min<sup>-1</sup>. These conditions were chosen based on the work by Monti and Baiker<sup>4</sup>. Moreover, the released water was collected in a trap cooled to 243 K and mounted between the reactor and the thermal conductivity detector.

### Temperature-Programmed Oxidation (TPO)

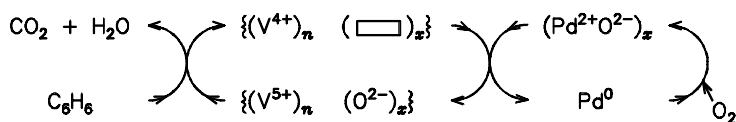
A helium-oxygen mixture (the flow rate 24 ml min<sup>-1</sup>) was applied in this case. The samples (0.2 g) were heated at the rate 15 K min<sup>-1</sup>. A glass thermal conductivity detector with platinum filaments was used for these experiments. TPO runs were conducted both with fresh samples and the samples after TPSR measurements, and after the catalyst had been subjected to the reaction for a given period. The apparatus and experimental conditions were described in detail elsewhere<sup>2</sup>.

### Electron Spin Resonance Spectroscopy (ESR)

The measurements were carried out simultaneously with the TPO experiments. This was made possible by the use of a demountable quartz reactor equipped with teflon stopcocks. All the spectra were recorded on a Bruker 200 D spectrometer.

## RESULTS AND DISCUSSION

The results of our previous studies<sup>1,2</sup> have led to the following scheme of the complete benzene oxidation (Scheme 1). The use of various techniques allowed us to propose the single processes shown in the scheme. Experimental data obtained in the present work will be evaluated from these aspects.



SCHEME 1

*Temperature-Programmed Surface Reaction*

We made an attempt to model the complete benzene oxidation shown at the left hand side of the scheme. Figure 1 shows the results of TPSR measurements. It is seen that only one peak with  $T_{\text{max}}$  in the 723 – 753 K range was observed with the AlO, PdAlO, and VAlO samples whereas the PdVAIO catalyst gave rise to an additional peak with  $T_{\text{max}} = 597$  K. This indicates that the concurrent presence of vanadium and palladium in the system gives rise to new active sites at the catalyst surface.

Gas chromatographic data on the samples are presented in Table I. They show that the nonadsorbed part of the pulses over AlO and PdAlO samples contained only ben-

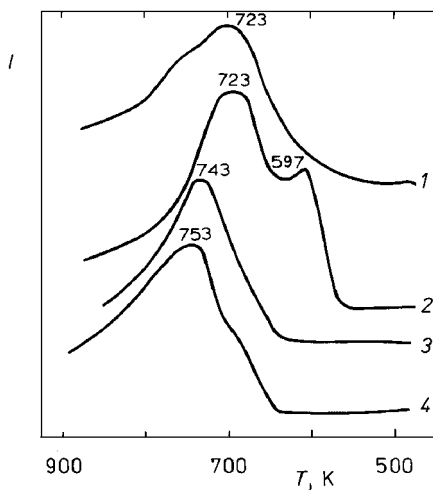


FIG. 1  
TPSR spectra ( $I$  = detector response) of different samples: 1 VAIO, 2 PdVAIO, 3 PdAlO and 4 AlO. The sensitivity in case 3 was four times and in case 4 twice higher than that of 1 and 2

TABLE I  
TPSR data on benzene interaction ( $B_{rev}$  reversible benzene,  $B_{ad}$  adsorbed benzene, Ox oxidation products,  $B_{irrev}$  irreversible benzene; all data in  $g\ S_{cat}^{-1} \cdot 10^{-3}$ )

Sample <sup>a</sup>	Run	Benzene adsorption and reaction at 523 K										Thermodesorption	
		1st pulse		2nd pulse		3rd pulse <sup>b</sup>		$\Sigma C_6H_6^c$	$B_{rev}$	$B_{irrev}$			
		$B_{rev}$	$B_{ad}$	Ox	$B_{rev}$	$B_{ad}$	Ox			$B_{rev}$	mild oxidn.	complete oxidn.	
AlO	1	2.78	1.61	—	3.98	0.41	—	4.39	2.02	—	—	—	—
PdAlO	1	1.58	2.81	—	3.94	0.45	—	4.39	3.26	—	—	—	—
VAlO	1	2.37	1.64	0.38	3.38	1.01	—	4.39	2.65	0.015	0.015	2.62	—
	2	2.99	1.40	—	4.39	—	—	4.39	1.40	0.04	0.015	1.35	—
	3	3.83	0.56	—	4.39	—	—	4.39	0.56	0.04	0.015	0.50	—
PdVAIO	1	0.77	2.87	0.75	3.70	0.44	0.25	4.39	3.31	0.18	0.001	3.13	—
	2	3.70	0.69	—	3.83	0.56	—	4.39	1.25	0.006	—	1.24	—
	3	4.17	0.22	—	4.39	—	—	4.39	0.22	0.004	—	0.22	—
PdVAIO	1	1.15	2.54	0.70	3.85	0.34	0.20	4.39	2.98	0.16	—	2.82	—
	2 <sup>d</sup>	4.00	0.39	—	4.39	—	—	4.39	0.39	0.30	—	—	—

<sup>a</sup> Designation of samples see Experimental. <sup>b</sup> Adsorbed benzene and oxidation products were not detected. <sup>c</sup> After 3rd pulse. <sup>d</sup> Regenerated sample. <sup>e</sup> Traces.

zene, while the analysis of thermodesorption products indicated only the presence of the reversibly adsorbed benzene.

Three successive cycles were carried out over VAIO sample, each involving benzene adsorption at 523 K until saturation and a subsequent thermal desorption from 523 to 813 K. The cycle was repeated after cooling the sample to 523 K.

Gas chromatographic analysis of the nonadsorbed part of benzene pulses admitted to the fresh VAIO sample at 523 K indicated the presence of oxidation products only after the first pulse. Each subsequent pulse gave a decreased amount of adsorbed benzene, the oxidation product formation being suppressed. No products of mild oxidation were found during next two successive runs.

Thermodesorption data confirmed the presence of the reversibly adsorbed benzene and of the products of mild and complete oxidation. This documents the occurrence of three types of active sites on the surface. Furthermore, changes in the amount of the TPSR species upon each subsequent run were consistent with the diminished amounts of the desorbed species and with the marked decrease in the products of the complete oxidation in particular.

Similarly to the VAIO sample, three successive cycles were performed with PdVAIO sample, which involved benzene adsorption until saturation and the subsequent thermodesorption. Gas chromatographic analysis of the nonadsorbed part of benzene pulses (applied to saturate the sample) revealed that the oxidation products occurred after the first and second pulse, and their total amount exceeded about three times the amount detected with the VAIO sample.

Two thermodesorption peaks were observed with PdVAIO catalyst, with maxima at 597 and 723 K. The TPSR species were analyzed separately for both peaks. Data are summarized in Table I. It is seen that the amount of benzene adsorbed on the PdVAIO surface was considerably larger than that on VAIO sample. The same trend was observed also for thermodesorption products of the complete oxidation. Since these runs were conducted under inert atmosphere (helium), the oxidation products were probably formed at the expense of the lattice oxygen from the vanadium oxide phase. Furthermore, these experimental data were compared with the statement that the introduction of palladium facilitates the complete oxidation of the hydrocarbon. During the following TPSR runs the amount of the desorbed species was drastically reduced, which can be related again to the lack of mobile oxygen in the vanadium oxide lattice.

Parallel runs were also carried out in which oxygen pulses were introduced at 573 K after the first adsorption–thermodesorption cycle. In this case the analysis indicated the presence of organic products in amounts of about  $0.012 \cdot 10^{-3} \text{ g g}_{\text{cat}}^{-1}$ . This finding shows that the decreased amounts of oxidation products found after next two cycles are not due to coking, but rather because of the depleted part of the lattice oxygen.

After the third cycle, two additional cycles were performed with the regenerated PdVAIO catalyst obtained by its heating for 3 h at 573 K in a flow of air. The results

are presented in Table I. Similar data were obtained with both the fresh and regenerated samples. Concerning the second cycle, the oxidation product formation on the regenerated sample was insignificant. This shows that the regeneration of the surface is not complete, i.e. that the lattice oxygen of the vanadium oxide phase is not fully restored.

### Temperature-Programmed Reduction

Figure 2 shows TPR patterns of VAIO and PdVAIO samples. Blank experiments with PdAlO convincingly showed that the palladium reduction as well as the hydrogen desorption from metallic palladium were complete around 423 K. The VAIO sample produced a TPR peak with  $T_{\max}$  at 803 K whereas PdVAIO gave rise to a peak with  $T_{\max} = 413$  K. Most likely, during TPR measurements in the presence of palladium, the dihydrogen species is dissociated to atomic hydrogen, the latter being much more reactive<sup>5,6</sup>.

The drastic fall of the reduction temperature confirmed once again that the introduction of palladium to VAIO system facilitates redox transitions between oxidation states of vanadium, in accordance with the mechanism of the complete benzene oxidation presented in Scheme 1. As reported earlier<sup>1</sup>, the activation of hydrogen on palladium through dissociative adsorption cannot be ruled out. In this case, the released atomic hydrogen, too, takes part in the reduction of V<sup>5+</sup> to V<sup>4+</sup>.

### Temperature-Programmed Oxidation

Following TPSR runs, TPO experiments with VAIO and PdVAIO samples showed that the oxidation of PdVAIO catalyst proceeded in the lower temperature range. This supports the facilitated redox transitions of vanadium in the presence of palladium (Fig. 2).

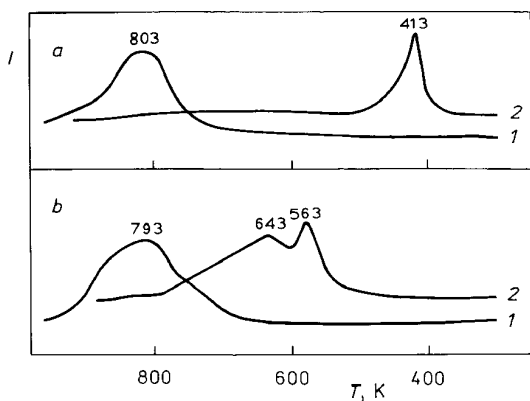


FIG. 2

TPR (a) and TPO (b) spectra of VAIO (1) and PdVAIO (2) samples. The TPR spectrum 2 was recorded at four times higher sensitivity

To identify changes in vanadium components of the system during temperature-programmed oxidation, TPO study combined with ESR spectroscopy could be useful.

Figure 3 shows TPO spectra of the fresh PdVAIO sample and of the same sample after a certain performance period for the following conditions: operation temperature 673 K, air space velocity  $330 \text{ h}^{-1}$ , and the gas phase benzene concentration ca  $90 - 98 \text{ g m}^{-3}$  (ref.<sup>2</sup>). A common feature of TPO spectra obtained was the presence of a low-temperature peak with  $T_{\text{max}}$  at 553 K (fresh sample) or in the 443 – 458 K region (in all the other cases). A second peak with  $T_{\text{max}} = 603 - 623 \text{ K}$  of the fresh PdVAIO sample appeared after 3 h treatment with benzene–air mixture. In subsequent runs, the peak maxima shifted to the higher temperatures, and in some cases another peak appeared with  $T_{\text{max}}$  at 723 K.

In order to interpret TPO data in more detail, ESR spectra were recorded after the low-temperature and high-temperature peaks shown in Fig. 3. A low-intensity, poorly resolved ESR spectrum of  $\text{V}^{4+}$  ions<sup>1</sup> was acquired with the fresh sample treated with helium flow in the cell. After treatment with benzene–air mixture under working conditions at 673 K, a well resolved signal due to the paramagnetic  $^{51}\text{V}^{4+}$  ( $3d_1$ ,  $I = 7/2$ ) has appeared<sup>7,8</sup> in the spectrum (Fig. 4, curve 1).

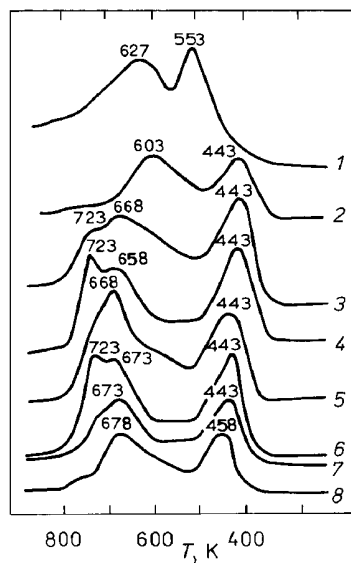


FIG. 3

TPO spectra of PdVAIO samples after operation under working conditions (see Experimental). Reaction period (h): 1 0 (fresh), 2 3, 3 6, 4 9, 5 12, 6 16, 7 21, 8 25

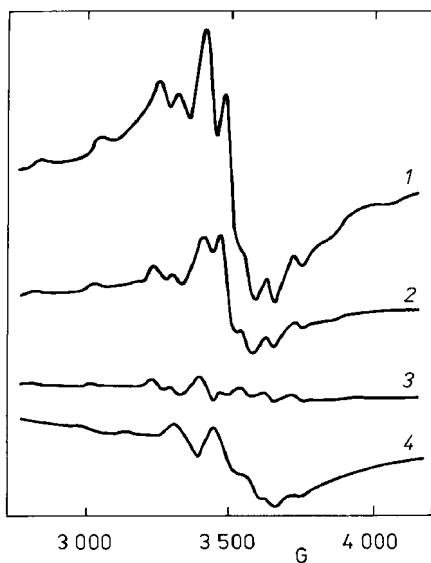


FIG. 4

ESR spectra of PdVAIO samples: 1 after 3 h-catalyst operation in argon–hydrogen, 2 after 1st peak of TPO experiment, 3 after 2nd peak of TPO experiment, 4 after 12 h-catalyst operation in argon–hydrogen

Since similar ESR spectra were registered irrespective of the operation time, the PdVAIO sample pattern shown in Fig. 4 refers only to 3 h-operation followed by TPO run. After TPO measurement had been conducted up to 533 K (the low-temperature region), the ESR signal of V<sup>4+</sup> ions showed decreased intensity (Fig. 4, curve 2), whereas above 733 K (high-temperature range) it disappeared (Fig. 4, curve 3). Therefore, TPO peaks can be attributed to the oxygen consumption in the oxidation of V<sup>4+</sup> to V<sup>5+</sup> ions. This models processes taking place according to the right hand side of Scheme 1. The pronounced shift of  $T_{\max}$  of the low-temperature peak (by about 100 K) due to the action of the redox mixture corroborated the fact that during the initial period of the catalyst operation, there proceeds formation of vanadium oxide phases of clustered V<sup>4+</sup> ions which readily take part in the redox process. These entities are also responsible for the high catalytic activity of the PdVAIO system in the complete oxidation of benzene. The clustered V<sup>4+</sup> ions can also be identified by the ESR spectrum of the sample treated with the reaction mixture (e.g. 12 h, Fig. 4, curve 4). A very broad line ( $\approx 2\ 000$  G) observed can be assigned to an enhanced dipole-dipole coupling between clustered V<sup>4+</sup> ions<sup>1,7,9,10</sup>.

The consumption of oxygen at 603 – 623 K can be associated with the single V<sup>4+</sup> ions difficult to oxidize and/or small-sized clusters. The high-temperature consumption of oxygen,  $T_{\max} = 723$  K, can be ascribed to the oxidation of V<sup>4+</sup> ions dissolved in the alumina lattice. These ions can be identified with the hyperfine structure of the ESR spectrum that is superimposed on the broad line.

## CONCLUSIONS

The following conclusions emerge from this study:

1. TPSR reaction measurements with the alumina-supported palladium-vanadium pentoxide catalysts demonstrated unambiguously the existence of an additional thermodesorption peak at the lower temperature region, in contrast to the other investigated samples. This catalyst produced the largest amounts of oxidation products even at admission of benzene pulses at 523 K, and the largest amounts of the products of mild and complete oxidation on raising gradually the reaction temperature.

2. TPR experiments showed that the introduction of palladium results in a considerable temperature fall of the vanadium oxidation state transitions. Facilitation of these transitions due to palladium was also confirmed by TPO measurements.

3. TPO study combined with ESR spectroscopy, performed after different periods of the catalyst exposure to the argon-hydrogen mixture, indicated that vanadium oxide phases and clustered V<sup>4+</sup> ions are formed which are supposed to be responsible for the high catalytic activity of the system.

Thus, in our opinion, the present study provides an additional support for the previously proposed mechanism<sup>1</sup> of the complete benzene oxidation over complex Pd-V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts.



## REFERENCES

1. Vassileva M., Georgieva S., Andreev A., Kotsev N., Shopov D.: *C. R. Acad. Sci. Bulg.* *36*, 1547 (1983).
2. Vassileva M., Andreev A., Dancheva S., Kotsev N.: *Appl. Catal.* *49*, 125 (1989).
3. Kotsev N., Shopov D.: *Commun. Dep. Chem. Bulg. Acad. Sci.* *15*, 61 (1982).
4. Monti D., Baiker A.: *J. Catal.* *83*, 323 (1983).
5. Nowak E. J.: *J. Phys. Chem.* *73*, 3790 (1969).
6. Batley G. E., Ekstrom A., Josen D. A.: *J. Catal.* *34*, 368 (1974).
7. Sharma V., Wokan A., Baiker A.: *J. Phys. Chem.* *90*, 2715 (1986).
8. Jonson B., Bendenstorf B., Larson L., Andersson S. L., Lundin S. T.: *J. Chem. Soc., Faraday Trans. 1* *82*, 767 (1986).
9. Nag N. K., Chary K. V. R., Reddy B. M., Rama Rao B., Subrahmanyam V. S.: *Appl. Catal.* *9*, 225 (1984).
10. Takahashi H., Shiotani M., Kobayashi H., Shoma Y.: *J. Catal.* *14*, 134 (1969).