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IMPROVEMENT OF AUTOMOTIVE EXHAUST CATALYSTS BY SUPPORT AND ELECTROCHEMICAL MODIFICATION INDUCED PROMOTIONAL EFFECTS

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Metal-support interactions can play an important role in catalytic oxidations and in the performance of *three-way automotive exhaust catalysts*. In this investigation the kinetics of CO and C_2H_4 oxidation and NO reduction by CO were studied on different model catalysts, Pt, Pd and Rh supported on different supports, SiO_2, γ-Al_2O_3, ZrO_2 (8% Y_2O_3), TiO_2 and TiO_2 (4% WO_3). Significant support effects in turnover frequency were observed for many of these metal-support combinations for all three model reactions. Some of these catalysts presented *nonlinear behavior* with rate oscillations in a wide range of reactants concentration.

In a separate set of experiments the kinetics of C_2H_4 oxidation were investigated on polycrystalline Rh films interfaced with ZrO_2 (8 mol% Y_2O_3) solid electrolyte (YSZ) in a galvanic cell of the type: C_2H_4,O_2,Rh/YSZ/Pt, O_2. It was found that by applying external potentials and thus supplying O^{2-} to the catalyst surface, up to 80-fold, increases in catalytic rate can be obtained (NEMCA effect). It was noted that the observed kinetic behavior upon increasing catalyst potential parallels qualitatively the observed increase in turnover frequency of Rh for C_2H_4 oxidation upon varying catalyst support.

1. INTRODUCTION

It has often been demonstrated in the literature that the effect of the support on the performance of metal catalysts can be very significant. The chemisorptive and catalytic properties of metal crystallites can be influenced by the nature of the carrier employed in catalyst formulation. This kind of metal-support interactions was first established by the early work of Schwab [1] and Solymosi [2] who attributed these phenomena to changes in the electronic state of the metal via electronic-type interactions with the carrier. In recent years, interactions of Group VIII metals with TiO_2 supports induced by high-temperature reduction were described under the concept of SMSI [3] and were shown to originate from migration of TiO_x species to the surface of the metal crystallites [4] and from an electronic factor operating concomitantly [5].

More recently it has been found that incorporation of altervalent cations into the crystal structure of semiconductive carriers can play an important role in defining the catalytic properties of the supported metal crystallites [6,7,9,10]. According to proposed explanations, these effects are due to electronic interactions at the metal-support interface caused by the different Fermi levels of the two solids in contact. For example, it was shown [6,7] that small Pt particles supported on TiO_2 doped with higher valence cations (Sb^{5+}, Ta^{5+}, W^{6+}) exhibit significantly reduced chemisorption capacity for H_2, O_2 and CO, because of the acceptance of charge transferred from the carrier to the Pt crystallites. However, the effect of higher valence doping of TiO_2 on the catalytic performance of Rh is opposite to that observed on Pt. Solymosi et al. [8] obtained enhanced activities for CO hydrogenation when Rh was supported on TiO_2 (W^{6+}). The same behavior was observed by Ioannides and Verykios [9,10] for CO, CO_2 and benzene hydrogenation, using Rh/TiO_2 (W^{6+}) catalysts.

Many investigators have found that the choice of support can affect the activity and stability of catalysts for several reacting systems. Vannice et al [11] observed that the type of the support can affect the behaviour of Pt catalysts for CO and CO_2 methanation, since higher activities were obtained when the metal was supported on TiO_2 rather than on Al_2O_3 or SiO_2. Metcalfe and Sundaresan [18] reported that Rh/YSZ is more active than Rh/Al_2O_3 for the CO/O_2 and CO/NO reactions and more recently Oh [13] found that a modified $Rh/CeO_2/Al_2O_3$ catalyst resulted in higher activities for NO reduction by CO than the Rh/Al_2O_3 catalyst. Different supports affect not only catalyst activity but also catalyst stability. For instance, Yao et al. [14] reported that the stability of Rh/ZrO_2 catalysts was considerably better than that of Rh/Al_2O_3, under H_2+NO reaction conditions.

The trends mentioned above can be important in the case of automotive emission-control catalysts. By using suitable supports, it is possible to achieve the same catalyst performance with smaller amounts of noble metals. The latter is crucial for Rh which is an expensive and scarce metal [15].

The use of solid electrolytes as active catalyst supports to induce the effect of Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA) [16] or in situ controlled promotion [17] and alter the catalytic properties of metal catalysts has been described in detail previously [16-18]. A goal of the present work was to explore the possible relationship between the NEMCA effect [16-18] and the effect of dopant-induced-metal-support interactions [6,7,9,10].

2. EXPERIMENTAL

Materials: Rh, Pd and Pt catalysts were prepared by impregnation of the supports with a solution of $Rh(NO_3)\cdot 2H_2O$, $PdCl_2$, H_2PtCl_6 (Alfa Products) respectively, to yield 0.5 wt% metal loadings. The following powder supports were used: SiO_2 (Alltech Associates), TiO_2 (Degussa P25), ZrO_2 (8 mol% Y_2O_3) (Zirconia Sales) and γ-Al_2O_3 (Akzo Chemicals).The dopant material for TiO_2 supports was WO_3 (Alfa Products). The doped and undoped TiO_2 supports were thermally treated (5h, 900°C-rutile form) while the ZrO_2 (8% Y_2O_3) support had undergone thermal pretreatment at 1500°C during production.

Before any measurements, the catalysts were reduced in a quartz tube by He flow (80 cc/min) at

250°C for 1 h followed by H_2 flow (80 cc/min) at 400°C for 1 h.

Catalyst characterization: The characterization of the catalysts was carried out in a BET apparatus (Accusorb 2100E, Micromeritics) with H_2 chemisorption and N_2 and/or Ar physical adsorption experiments at 77 K.

Electrochemical measurements: The basic experimental setup is shown schematically on Fig. 1a. The metal working catalyst electrode is deposited on the surface of a ceramic solid electrolyte (i.e. Y_2O_3-stabilized-ZrO_2 (YSZ), an O^{2-} conductor). Details of catalyst, counter and reference electrode preparation and characterization have been reported in detail elsewhere [16]. The catalyst electrode is exposed to the reactive gas mixture (i.e. C_2H_4+O_2) in a continuous flow gradientless reactor. Under open-circuit conditions (I=0) it acts as a regular catalyst for the C_2H_4 oxidation reaction. The electrodes are connected with a galvanostat/potentiostat which is used to apply constant currents between the catalyst and the counter electrode or constant potentials between the catalyst and reference electrode. In this way O^{2-} ions are supplied from (or to) the solid electrolyte to (or from) the catalyst-electrode surface. The current is defined positive when anions are supplied to the catalyst electrode.

Apparatus: The catalysts were tested under reaction conditions in the experimental setup shown in Fig. 1b. Two types of reactors where used, one for the supported catalysts, and one for the NEMCA experiments. Experimental details for the latter have been reported elsewhere [16]. Both reactors have been shown to behave as CSTR.

Reaction systems: The reactions used for catalyst testing are the main ones which take place in a catalytic converter, i.e.: CO oxidation, C_2H_4 oxidation (as a model light HC) and NO reduction by CO. Experiments were conducted within the temperature range of 150-500°C.

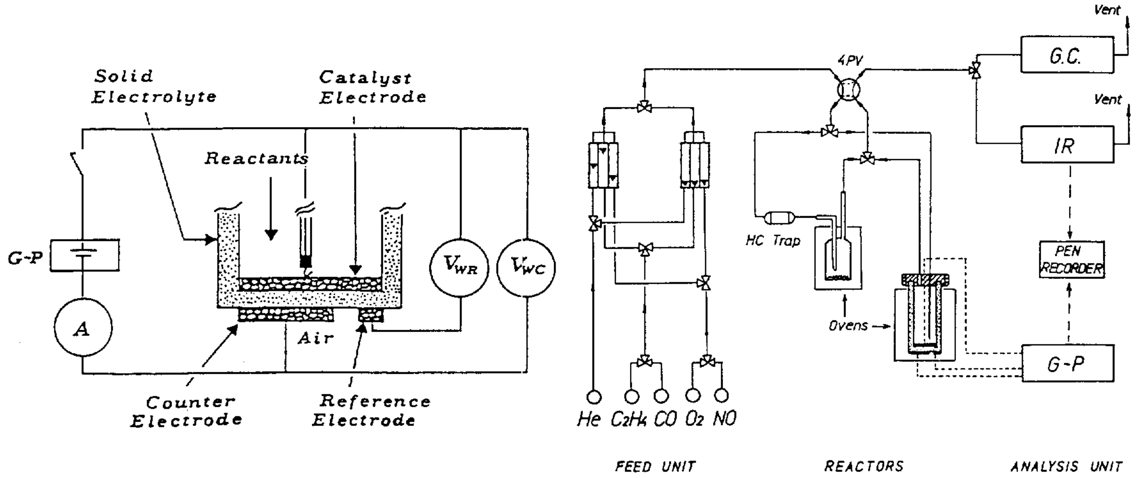

Fig. 1. a) The three electrode configuration used in the NEMCA experiments.
b) Experimental set-up for catalytic and NEMCA experiments.

3. RESULTS AND DISCUSSION

3.1. Catalyst characterization

The results for all fifteen catalysts tested are summarized in Table 1. The H/M ratio (M: Rh, Pd, Pt) was calculated assuming a 1:1 H to metal stoichiometry.

Table 1. Catalyst characterization

	DISPERSION [H/M] (*)			BET SURFACE AREA (**) (m^2/gr)	BET SURFACE AREA (***) (m^2/gr)
	Rh	Pt	Pd		
$ZrO_2(8\%Y_2O_3)$	0.44	0.44	0.37	1.55±0.04	5.2±0.6
TiO_2	0.10	0.07	0.33	Ø	0.13±0.02
$TiO_2(4\%WO_3)$	0.30	1.00	0.33	Ø	4.9±0.9
γ-Al_2O_3	1.00	0.68	0.61	177.1±1.2	Ø
SiO_2	0.65	0.54	0.65	261.7±2.2	Ø

(*) H_2 chemisorption at 298 K, (**) N_2 physical adsorption at 77 K, (***) Ar physical adsorption at 77 K

3.2. CO oxidation

The kinetics of the CO oxidation reaction over all three noble metals exhibit a Langmuir-Hinshelwood type behavior, due to competitive adsorption of CO and oxygen, characterized by the appearance of rate maximum with increasing CO partial pressure. This is a typical behavior which has been described by many investigators for this reaction system [19,20]. The catalytic activity, presented as turnover number of CO_2 production, was measured by varying either the partial pressures of CO or O_2, or temperature, keeping the other parameters constant.

An example of comparative representation of catalytic activity under CO oxidation is given in Fig. 2. This figure shows the dependence of the rate (turnover number) on the partial pressure of CO and refers to 0.5 wt% Rh supported on different carriers. It can be observed that catalytic activity is enhanced when the metal is supported on the doped carriers, ZrO_2 (8% Y_2O_3) and TiO_2 (4% WO_3). The rates of CO consumption over Rh/ZrO_2 (8% Y_2O_3) and Rh/TiO_2 (4% WO_3) are significantly higher than those observed when Rh is supported on high surface area γ-Al_2O_3, which is the commercially used support. Furthermore, the beneficial effect of doping of the support is obvious, upon comparing the curves corresponding to the two TiO_2 supports (doped and undoped). A similar beneficial effect upon doping the TiO_2 support with W^{6+} cations was also observed in the case of Pd while the opposite effect was observed in the case of Pt.

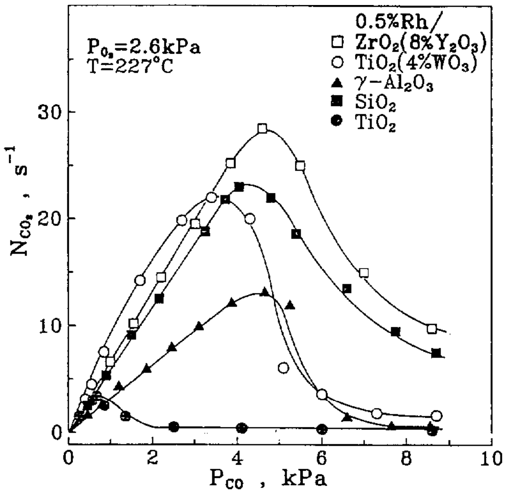

Fig. 2. Activity of supported Rh catalysts under CO oxidation.

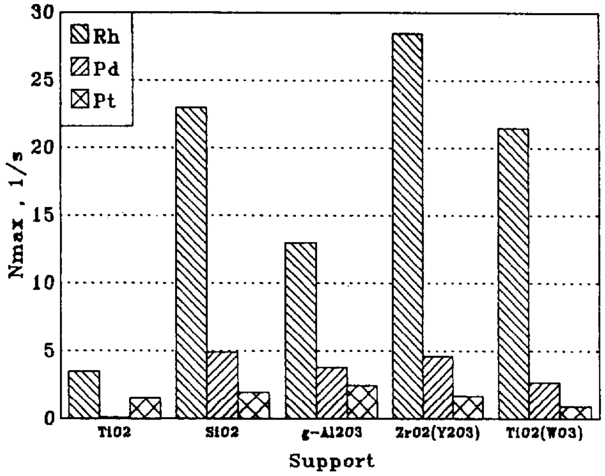

Fig. 3. Maximum measured turnover frequencies for CO oxidation (corresponding to the r maxima of r vs P_{CO}) at T=227°C and P_{O_2}=2.6 kPa.

A comparison of the intrinsic activity of all fifteen catalyst formulations, tested under CO oxidation reaction conditions, is given in the bar diagram of Fig. 3 which shows the maximum measured turnover numbers at 227°C and oxygen partial pressure of 2.6 kPa. Rhodium is clearly a far superior CO oxidation catalyst as compared to Pt and Pd, in accordance with results of other investigators [21]. It is also observed in Fig. 3 that the activity of Rh for CO oxidation is very sensitive to the carrier employed for its dispersion. A weaker sensitivity is exhibited by Pd and Pt.

3.3. C_2H_4 oxidation

The kinetics of this reaction were also found to follow a Langmuir-Hinshelwood type behavior, with competitive adsorption of C_2H_4 and oxygen. A comparative kinetic diagram for all the supported Rh catalysts is given in Fig. 4. The dashed lines indicate an abrupt drop in the ethylene combustion rate which is probably due to surface oxide formation. The same behavior was also observed in the electrochemical promotion (NEMCA) experiments, as briefly discussed below and further described elsewhere [22]. The highest combustion activities were obtained over Rh/$TiO_2(WO_3)$ and Rh/YSZ catalysts. The beneficial effect of doping the TiO_2 carrier with W^{6+} cations is also illustrated in Fig. 4. The enhancement of the ethylene combustion activity of Rh when it is dispersed on W^{6+} doped TiO_2 is particularly pronounced at higher oxygen partial pressures ($P_{O_2} > 1$ kPa).

Regarding the Pd and Pt catalysts supported on the same substrates, the following behavior was recorded: Higher activities were observed upon doping the TiO_2 supports with W^{6+} in the case of Pd catalysts, while the inverse behavior was observed in the case of Pt catalysts. Pd/YSZ is significantly better than Pd/γ-Al_2O_3. The Pt/YSZ, and Pt/γ-Al_2O_3 exhibited the best activity among the Pt catalysts.

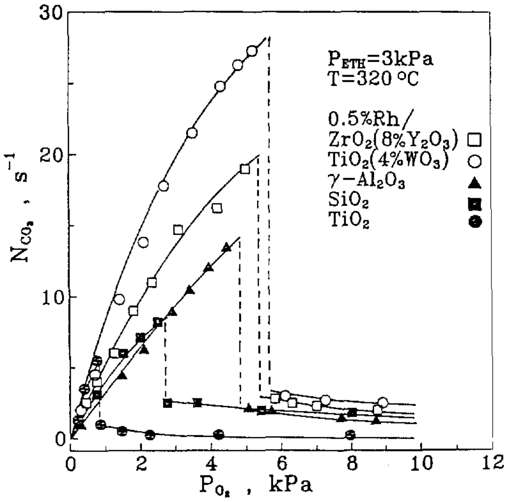

Fig. 4. Effect of P_{O_2} and support on the rate of C_2H_4 oxidation on supported Rh.

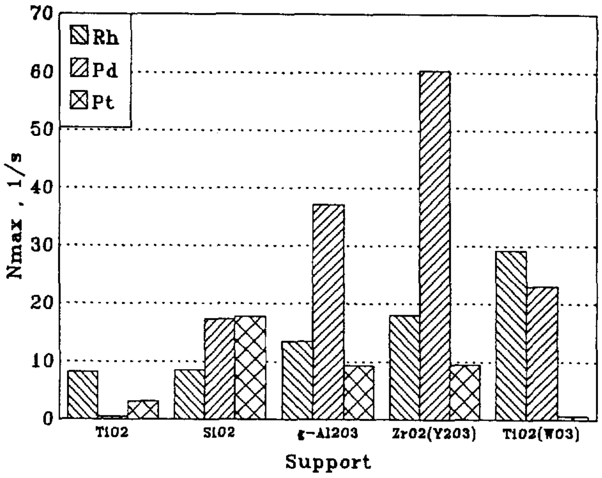

Fig. 5. Maximum measured turnove frequencies of C_2H_4 oxidation at T=320°C, $P_{C_2H_4}$=3 kPa.

A comparative summary of these results concerning C_2H_4 oxidation is given in Fig. 5. It is worth noting the superior activity of Pd supported catalysts for this reaction, in agreement with results reported in the literature [23,24]. The best carriers for the different metals are $TiO_2(W^{6+})$ for Rh, $ZrO_2(Y_2O_3)$ for Pd and SiO_2 for Pt.

3.4. CO-NO reaction

The removal of NO_x is of great interest for air pollution control and thus extended research has been carried out during the past fifteen years in the reduction of NO by CO. In the present study, the activity of Pt, Pd and Rh for NO reduction by CO was investigated and the influence of the carrier was examined. It was found that, in addition to CO_2 and N_2 formation, N_2O was also formed in appreciable quantities. The N_2O production rate was found to go through a maximum with increasing temperature, in the range of 320-350°C, due to decomposition of N_2O at higher reaction temperatures [25,26].

The influence of the carrier on NO reduction activity of Pt, Pd and Rh catalysts is illustrated in Fig. 6. It is apparent that, in agreement with results of earlier studies [21,27], among the three metals, Rh exhibits far superior NO reduction activity in the presence of CO. The activity of Rh is also sensitive to the support employed for its dispersion. Thus, Rh dispersed on W^{6+} -doped TiO_2 exhibits activity which is approximately 4 times higher than that of Rh on undoped TiO_2, while the activity of Rh on the other supports investigated falls in between.

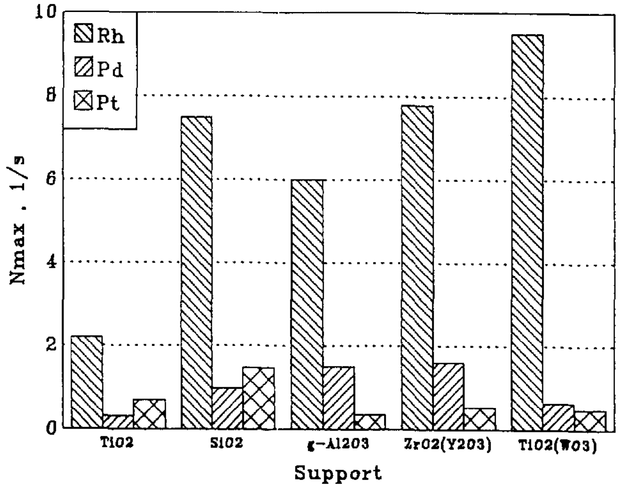

Fig. 6. Maximum measured turnover frequencies for the CO-NO reaction at T=360°C, P_{NO}=1 kPa.

3.5. NEMCA studies for the system $C_2H_4/O_2/Rh$

The kinetics of C_2H_4 oxidation were also investigated on polycrystalline Rh films interfaced with ZrO_2 (8 mol% Y_2O_3), or YSZ solid electrolyte in a galvanic cell of the type: C_2H_4, O_2, Rh/YSZ/Pt, O_2. It was found that by applying external potentials and thus supplying O^{2-} to the catalyst surface, up to 80-fold increases in catalytic rate are obtained.

An example is shown in Fig. 7 which shows a typical galvanostatic transient, i.e., it depicts the transient effect of a constant applied current on the rate of C_2H_4 oxidation and on catalyst potential, V_{WR}. At the start of the experiment ($t \leq 0$) the circuit is open (I=0) and the steady state catalytic rate value, r_o, is 1.8×10^{-8} g-at O/s. At t=0 the galvanostat is used to apply a constant current (I=400 μA) between the catalyst and the counter electrode. According to Faraday's Law, oxygen anions are supplied to the catalyst at a rate $G_O = I/2F = 2.05 \times 10^{-9}$ g-at O/s. This causes an 8800% increase in catalytic rate ($\Delta r = 1.6 \times 10^{-6}$ g-at O/s). The rate increase Δr is 770 times larger than the rate of oxygen anions G_O of supply (Λ=770). This means that each O^{2-} supplied to the catalyst causes, at steady state, 770 chemisorbed oxygen atoms to react and form CO_2. In the present work the maximum observed value of the enhancement factor (Faradaic efficiency) Λ [16-18] was of the order of 5×10^4.

The kinetic behavior upon varying catalyst potential is shown in Fig. 8. It is worth noting the similarities with Fig. 4. Increasing catalyst potential causes the same rate changes as variation of the catalyst support in the order TiO_2, SiO_2, γ-Al_2O_3, ZrO_2(8%Y_2O_3), TiO_2(4%WO_3). Since the NEMCA effect is due to the change in catalyst work function $e\Phi$ with changing catalyst potential ($\Delta e\Phi = e\Delta V_{WR}$) [16,18] and to the concomitant back-spillover of promoting oxide ions onto the catalyst surface [16,28], it is likely that the above catalyst support sequence corresponds to increasing work function of the supported Rh crystallites, i.e. $e\Phi$ is lowest for Rh supported on TiO_2 and highest for Rh supported on TiO_2(4%WO_3).

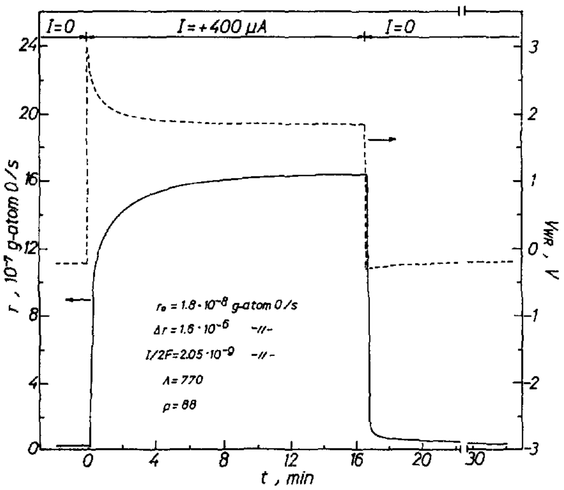

Fig. 7. A galvanostatic transient during C_2H_4 oxidation on Rh catalyst. T=350°C, P_{O_2} = 2 kPa, $P_{C_2H_4}$=5.5 kPa.

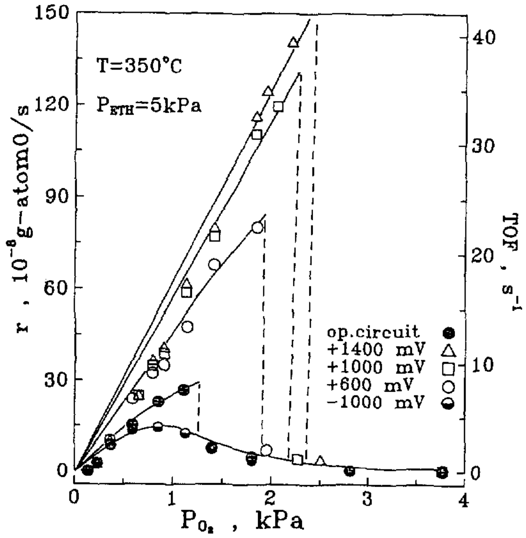

Fig. 8. Effect of P_{O_2} and catalyst potential on the rate of C_2H_4 oxidation on Rh.

4. CONCLUSIONS

It was found that the catalytic activity of three-way catalysts can be altered significantly by using different supports for each noble metal component. This may be due to electronic interactions between the metal and the support [9,10] and/or due to oxygen back spillover from the supports to the catalyst as in the NEMCA experiments [16-18,28].

The following sequence of catalytic activity was observed, with minor variations for each reaction:

Rh: TiO_2(4% WO_3)>ZrO_2 (8% Y_2O_3)>γ-Al_2O_3, SiO_2>TiO_2
Pd: ZrO_2(8% Y_2O_3)>γ-Al_2O_3>TiO_2(4% WO_3), SiO_2>TiO_2
Pt: SiO_2>ZrO_2(8% Y_2O_3), γ-Al_2O_3>TiO_2>TiO_2(4% WO_3)

Qualitatively similar results were obtained in the NEMCA study of C_2H_4 oxidation. It was shown that the catalytic rates and also the location of the abrupt break in the rate vs P_{O_2} curves (most likely corresponding to the formation of a surface oxide) can be adjusted by means of the externally applied potential. The observed strong similarities between the NEMCA effect [16-18] and the effect of dopant-induced-metal-support interactions [6,7,9,10] suggests that the origin of both effects may be similar. Surface spectroscopic and work function measurements could further elucidate this point.

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