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Linear Solvation Energy Relationship as a potential predictive tool to investigate catalytic properties: A study of perovskite materials in DeNO$_x$ and DeN$_2$O applications

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ABSTRACT

The Linear Solvation Energy Relationship approach has been developed in order to correlate adsorptive properties of LaCoO$_3$ perovskite based materials with their catalytic performances. Particular attention was paid to the influence of palladium incorporation according to two different routes: (i) a sol–gel method leading to oxidic palladium species homogeneously distributed in the bulk structure and (ii) a conventional wet impregnation route with a preferential segregation of palladium species at the surface. Substantial changes in the simultaneous catalytic decomposition of NO and N$_2$O were observed on LaCoO$_3$ with no meaningful NO conversion contrarily to N$_2$O. It has been found that the sol–gel method leads to significant improvement in N$_2$O conversion related to an enhancement of the hydrogen bond acceptor character predicted by the LSER approach. Subsequent predictions also revealed the strong affinity of water which was found to inhibit the rate of N$_2$O decomposition.

1. Introduction

Linear Solvation Energy Relationship (LSER) [1] has been previously reported as a suitable approach to investigate the adsorptive properties of carbonaceous materials [2] and more recently catalytic materials [3,4]. This theory allows the identification of the nature of interactions in gas–solid transfer processes and further quantifications based on a multiple regression analysis using experimental data from inverse gas chromatography. Hence, these investigations provided useful relationships between the surface energy contributions and the adsorptive behavior. However, the remaining question which arises from those previous investigations is probably related to further extrapolations to catalytic properties in order to conclude if the LSER theory can be considered as a robust predictive tool to discriminate over different types of catalysts the optimal one for selected applications.

This theory is based on Eq. (1). The gas–solid partition coefficients (K_c) can be estimated from adsorption isotherm at infinite dilution, i.e. at zero concentration by the elution of characteristic point method (ECP) earlier developed by Conder and Young [5].

$$\log_{10}(K_c) = c + rR_2 + s\pi_2^{\mathrm{H}} + a\sum\alpha_2^{\mathrm{H}} + b\sum\beta_2^{\mathrm{H}} + l\log_{10}L^{16} \qquad (1)$$

The free energy parameters ($\log_{10}K_c$) can be explained on the basis of five parameters [3,4]. R_2 represents for a selected solute, its capacity to interact through n- and π-electron pairs [6], π_2^{H} illustrates its dipolar/polarisable character [7], $\sum\alpha_2^{\mathrm{H}}$ its hydrogen-bond acidity or hydrogen-bond donor ability [8], $\sum\beta_2^{\mathrm{H}}$ its hydrogen-bond basicity or hydrogen-bond acceptor ability [7,8] and finally $\log_{10}L^{16}$ which represents its gas–liquid partition on hexadecane [9]. All those parameters can be estimated and experimental values are accessible using a data bank collecting approximately 3000 organic compounds. c is the constant of the regression and K_c is calculated as the ratio C_s/C_g where C_s is the concentration of the adsorbed solute on the solid phase and C_g its concentration in the gas phase when C_g tends towards zero (infinite dilution conditions).

Among the most interesting catalytic feature derived from this model, it was earlier found that NO$_2$ exposure leads to changes in the adsorptive properties of Diesel soot [4]. Herein, we have undertaken a combined experimental and theoretical study of a series of perovskite based materials in which special attention has been paid on their adsorptive properties and subsequent catalytic performances in the simultaneous decomposition of N$_2$O and NO. Particular attention was focused on surface changes after palladium incorporation. Two different routes were selected for Pd incorporation. According to both methods, the resulting materials exhibit different catalytic properties which have been discussed on the basis of their hydrogen-bond acceptor ability predicted by the LSER approach.

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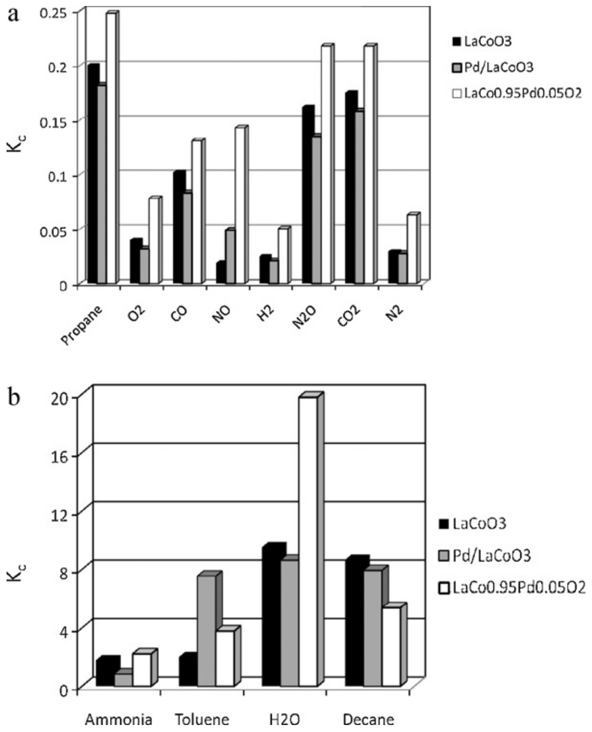

Fig. 1. Predicted K_c values of various gaseous compounds representative of usual exhaust gas composition from vehicle engines and stationary sources (a) and of various hydrocarbons compounds and water (b).

2. Experimental

2.1. Catalyst preparation and characterization

The preparation procedure of $LaCoO_3$ was described elsewhere [10,11]. A so-called sol–gel method involving a citrate route was implemented using cobalt and lanthanum nitrate salts dissolved in the presence of citric acid (CA) according to the molar CA/(Fe + La) ratio equal to 1. The solvent was then evaporated by heating at 60 °C under vacuum until the formation of a gel. After drying at 80 °C, the solid was successively heated at 200 °C to promote the decomposition of nitrates and calcined in air at 600 °C for 8 h. $LaCoO_3$ ($25\,m^2\,g^{-1}$) was impregnated by palladium nitrate solution with adjusted concentrations in order to obtain 1 wt.% Pd. Subsequent calcination in air at 400 °C led to $PdO_x/LaCoO_3$ labelled $Pd/LaCoO_3$. Alternately, 2.1 wt.% Pd was incorporated before the gel formation in order to get isolated oxidic Pd species stabilized inside the perovskite structure. After calcination in air at 600 °C, $LaPd_{0.05}Co_{0.95}O_3$ was obtained. X-ray diffraction (XRD) patterns were recorded on a HUBER G-670 diffractometer equipped with a Cu Kα ($\lambda = 0.154$ nm) radiation. XPS analysis was performed on a Kratos spectrometer equipped with a monochromatized aluminum source for excitation. Binding energy (B.E.) values were referenced to the binding energy of the C 1s core level (285 eV). H_2-temperature-programmed reduction experiments (H_2-TPR) were carried out in a Micromeritics Autochem II 2920 with 5 vol.% H_2 in Ar and a gradual heating rate of 5 °C/min.

2.2. LSER measurements

Experimental procedure for gas chromatography was described elsewhere [3,4] using a Varian GC 3800 chromatograph equipped with a TCD detector. The catalytic materials diluted with silanised glass beads were placed in a Teflon column of 20 cm long with an internal diameter of 2.1 mm heated at 50 °C under flowing He with a flow rate of $20\,mL\,min^{-1}$. The signals were recorded on a Diamir workstation.

2.3. Catalytic reaction

Temperature-programmed measurements were performed in a fixed bed flow reactor with a gradient temperature of $5\,°C\,min^{-1}$. The gas mixture was composed of 1000 ppm N_2O and 1000 ppm NO diluted in He. 0.7 g of catalyst in powder form was exposed to a total flow rate of $15\,L\,h^{-1}$, corresponding to a space velocity of approximately $10{,}000\,h^{-1}$. Inlet and outlet gas mixtures were analyzed using a µGC Varian CP-4900 chromatograph fitted with two thermal conductivity detectors. Prior to quantification, reactants and products were separated on two 5 Å molecular sieve and poraplot Q columns.

3. Results and discussion

3.1. LSER observations on $LaCoO_3$: related impact to Pd incorporation

Fig. 1 shows various solutes which usually compose exhaust gases from stationary and mobile sources. Adsorption isotherms were established for each solute on $LaCoO_3$ and Pd-modified $LaCoO_3$. LSER equations can be further used to predict affinity of gaseous compounds with the solid at a given temperature.

The optimized LSER values of the studied solids are reported in Table 1 for $LaCoO_3$, $Pd/LaCoO_3$ and $LaPd_{0.05}Co_{0.95}O_3$. As observed, $Pd/LaCoO_3$ is not able to interact through n- and π-electron pairs. The negative r-coefficient ($r = -0.83$) of $LaCoO_3$ means that some lone pair–lone pair repulsive interactions occur between the hydrocarbon in the gas phase and the solid material. The positive values for the coefficient s reflect the possibility of interactions between the surface and dipolar/polarisable probe. Owing the results, all the materials can interact through dispersive interactions (l-coefficient). The latter represents the occurrence of London forces, which are universal and all the gaseous compounds can interact through this type of interactions. Hydrogen-bond acceptor (a-coefficient) and hydrogen-bond donor (b-coefficient) characters are also evidenced in the series of catalysts.

As indicated in Table 1, parallel to an increase of the a-coefficient after Pd incorporation, a decrease of the b-coefficient is noticeable. Hence, the hydrogen bond acceptor property of $LaCoO_3$ would be enhanced in presence of Pd at the expense of the hydrogen-bond donor property. In fact, such a tendency seems markedly

Table 1
Comparison between LSER parameters and surface properties for the perovskite based materials.

Catalysts	$(Pd/La)_{bulk}$[a]	SSA[b] ($m^2\,g^{-1}$)	XPS analysis		LSER parameters				
			B.E. Pd $3d_{5/2}$ (eV)	$(Pd/La)_{surf}$[a]	r	s	a	b	l
$LaCoO_3$	–	15	–	–	–0.83	0.59	1.70	1.49	0.48
$Pd/LaCoO_3$	0.02	–	336.2	0.04	0	0.41	2.06	0.93	0.49
$LaPd_{0.05}Co_{0.95}O_3$	0.05	19	337.2	0.02	0.56	0.37	2.14	1.12	0.39

[a] Atomic ratio.
[b] Specific surface area.

accentuated on $LaPd_{0.05}Co_{0.95}O_3$ when isolated oxidic palladium species interact inside the structure. Affinities related to interactions between various molecules and the surface catalysts have been examined. The selected molecules are representative of the usual exhaust gas composition from vehicle engines and stationary sources. As exemplified in Fig. 1a, the calculated values for the gas–solid partition coefficient (K_c) remain lower than 1 revealing a low affinity between gaseous compounds and the materials in our operating conditions. However, it seems obvious that NO and O_2 have a poorer affinity than N_2O. Indeed, the studied catalysts can interact through all types of interaction and N_2O has the highest non-polar character ($\log L^{16}$ value), can interact through dipolar/polarisable forces unlike NO and O_2. Moreover, NO has the highest ability to interact through n- and π-electron pair interactions, thus the very weak adsorption on $LaCoO_3$ is due to repulsive interactions (negative r-value) while attractive interactions occur with $LaPd_{0.05}Co_{0.95}O_3$ because of positive value of the r-coefficient as mentioned in Table 1. These observations might reflect competitive adsorption in favor of N_2O with a weak inhibiting effect of NO and O_2 on the perovskite based materials. Fig. 1b also compare the affinity of various reducing agents useful for the reduction of NO_x. As observed, interactions between heavy hydrocarbons and $LaCoO_3$ should occur preferentially. Nevertheless, the most relevant information is connected to stronger interactions with water (the molecule with the highest hydrogen-bond donor value comparing the other tested compounds) which might significantly altered the catalysts efficiency essentially by site blocking.

3.2. Bulk and surface properties

Tentative comparisons in Table 1 can be achieved on the basis of bulk and surface analysis. As exemplified, XPS analysis highlights significant changes in B.E. values according the procedure used for Pd incorporation. Unexpected high value for the Pd $3d_{5/2}$ core level is recorded on $LaCo_{0.95}Pd_{0.05}O_3$ (337.2 eV vs. 336.8 eV on $Pd/LaCoO_3$) in comparison with the current value reported in the literature for Pd^{2+} species stabilized as PdO (336.2 eV [12]). Correlatively, impregnated $Pd/LaCoO_3$ catalyst exhibits a strong surface Pd enrichment ascribed to a preferential segregation of PdO clusters weakly interacting with $LaCoO_3$. Those spectral features earlier observed and discussed are well in agreement with the occurrence of strong interactions when isolated oxidic Pd species are stabilized inside the perovskite structure. Subsequent shift in the B.E. value can reflect an electron charge transfer from Pd to $LaCoO_3$ leading to a weakening of the Co–O bond [13]. H_2-TPR experiments support such an explanation. As observed in Fig. 2, a two-step reduction process is observed involving the intermediate formation of Co^{2+} on $LaCoO_3$. Let us notice that this reduction process occurs more readily in the presence of Pd and is slightly more accentuated on $LaCo_{0.95}Pd_{0.05}O_3$ than on $Pd/LaCoO_3$.

3.3. Catalytic decomposition of N_2O: tentative correlations with surface properties and LSER parameters

Catalytic measurements were subsequently performed from temperature-programmed experiments in the temperature range of 25–500 °C. TPR curves, recorded in the presence of 1000 ppm NO and 1000 ppm N_2O, are collected in Fig. 3. In the temperature range of the study, NO reduction does not take place as suggested by the LSER predictions. Then, qualitative estimation of the overall activity in the decomposition of N_2O has been obtained leading to the following sequence: $Pd/LaCoO_3 < LaCoO_3 < LaPd_{0.05}Co_{0.95}O_3$. Hence, Pd addition can contribute to a significant enhancement in N_2O conversion but strongly depends on the incorporation mode. As observed, the incorporation of Pd in the perovskite lattice by sol–gel procedure leads to the best catalytic performances which can be assigned to an enhancement of the hydrogen-bond acceptor character of the catalyst. Such observations seem to be well in agreement with XPS and LSER observations. As discussed elsewhere [13], the shift observed on the B.E. towards higher values highlights a weakening of the Co–O bond which originates greater oxygen mobility on $LaCo_{0.95}Pd_{0.05}O_3$. Subsequent O desorption at high temperature further releasing available sites for N_2O adsorption and decomposition could explain the rate enhancement in N_2O decomposition observed after Pd addition. Thus, the significant increase in the hydrogen-bond acceptor ability on $LaPd_{0.05}Co_{0.95}O_3$ would

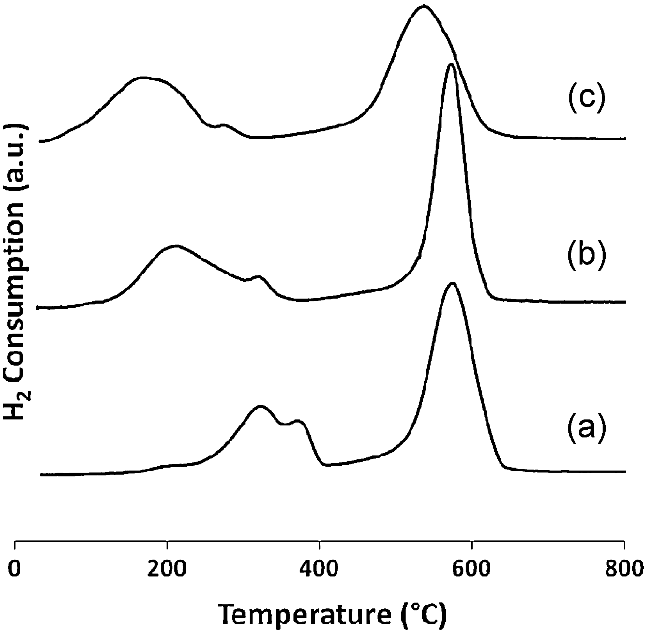

Fig. 2. H_2-temperature-programmed experiment of $LaCoO_3$ based catalysts: $LaCoO_3$ (a); $Pd/LaCoO_3$ (b); $LaPd_{0.05}Co_{0.95}O_3$ (c).

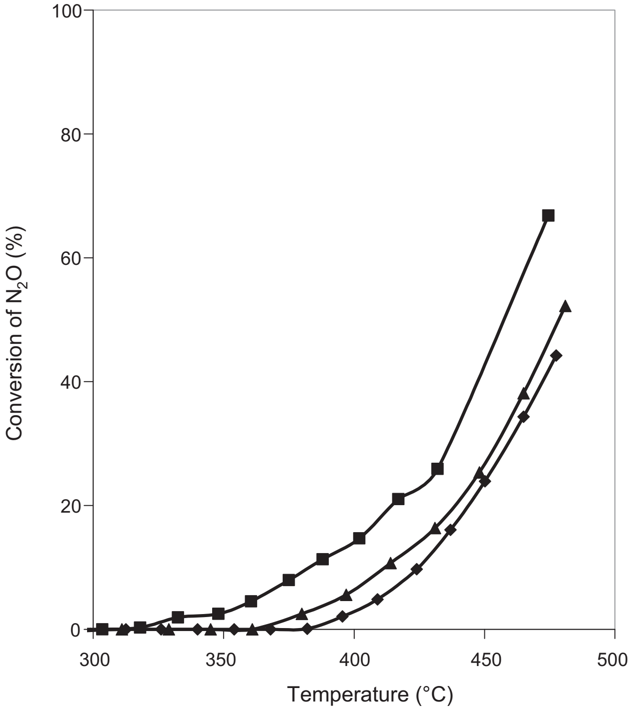

Fig. 3. Temperature-programmed N_2O decomposition in the presence of 1000 ppm N_2O and 1000 ppm NO: $LaCoO_3$ (▲); $Pd/LaCoO_3$ (♦); $LaPd_{0.05}Co_{0.95}O_3$ (■).

Table 2
Influence of water in the catalytic performances of Pd/$LaCoO_3$ in the decomposition of N_2O at 460 °C.

Reactive conditions	N_2O conv. (%)	Specific rate (mol h^{-1} g^{-1})	Apparent activation energy (kJ mol^{-1})
Dry conditions[a]	32	2.8×10^{-4}	55 ± 3
Wet conditions[b]	10	0.9×10^{-4}	50 ± 3

[a] 1000 ppm NO and 1000 ppm N_2O.
[b] 1000 ppm NO, 1000 ppm N_2O, 3 vol.% O_2 and 0.5 vol.% H_2O.

reflect a greater mobility and reactivity towards N_2O decomposition than on Pd/$LaCoO_3$. In this latter case such oxygen mobility would be restricted to the surface and would concern essentially the periphery of the palladium oxide particles. As exemplified in Fig. 4, a very good correlation between the estimates of K_c and N_2O conversion is obtained in agreement with the above-mentioned explanations.

Finally, the influence of water has been investigated. Prior to catalytic measurements, structural properties of Pd/$LaCoO_3$ have been assessed under wet atmosphere by *in situ* XRD measurements. As illustrated, Fig. 5 shows that the rhombohedral structure of $LaCoO_3$ is still preserved after exposure up to 3 vol.% H_2O for 2 h at 800 °C under wet atmosphere with no bulk detectable La_2O_3 and Co_3O_4 phases. As indicated in Table 2, water has a strong detrimental effect on the catalytic activity with a significant loss of conversion during water exposure. Apparent activation energies have been roughly calculated from TPR conversion. As seen, those vary within the margin of error suggesting that the loss of activity is mainly related to site blocking due to strong adsorption rather than subsequent alteration of active sites due to surface and bulk reconstructions (Table 2) which presumably occurred with modifications of the apparent activation energy [13]. Hence, on the basis of those comparisons between catalytic measurements and optimized data from the LSER approach, we can conclude that this theory can be profitably used for predicting the beneficial or detrimental effects of various molecules on the catalytic performances of DeN_2O catalysts.

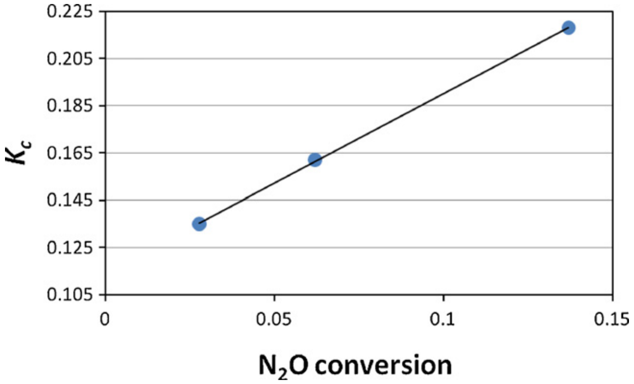

Fig. 4. Correlation between catalytic performance and LSER prediction.

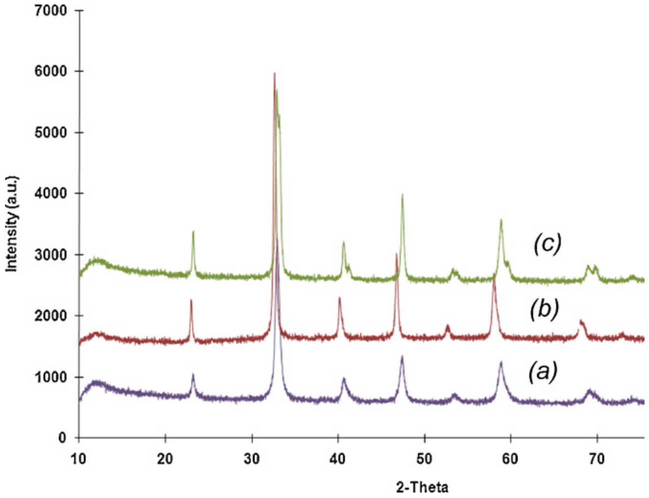

Fig. 5. *In situ* XRD measurements under wet atmosphere in the presence of air and 3 vol.% H_2O. Patterns recorded of Pd/$LaCoO_3$ at RT (a); after 2 h exposure at 800 °C under wet conditions (b); after cooling down at room temperature (c).

4. Conclusion

This study reports comparative data obtained from catalytic measurements on perovskite based materials ($LaCoO_3$) and adjusted values for various descriptors from the LSER approach on the basis of their adsorption isotherms which account for various types of interactions between different substrates and solutes representative of exhaust gas emissions from stationary and mobile sources. These results clearly demonstrate that LSER approach can be a powerful predictive tool as highlighted by the beneficial impact of $LaCoO_3$ hydrogen-bond acceptor properties further improved after Pd incorporation. This behavior could be connected to an increase in the mobility of oxygen lattice particularly when Pd is stabilized inside the perovskite structure as isolated cationic Pd species. Subsequent desorption with a rise in temperature would generate oxygen defects suitable for the adsorption and the subsequent dissociation of N_2O. The presence of water induces a significant loss of activity which has not been ascribed to alteration of the structural properties but mainly to competitive adsorptions in favor of water further poisoning the catalyst activity by site blocking.

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