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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_2O 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_2O were observed on $LaCoO_3$ with no meaningful NO conversion contrarily to N_2O. It has been found that the sol–gel method leads to significant improvement in N_2O 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_2O 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_2O 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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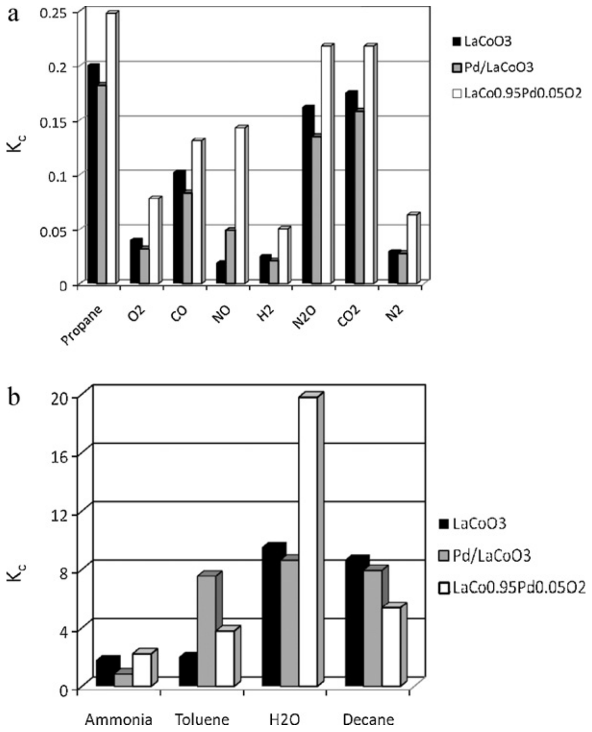

Fig. 1. Predicted K_c values of various gaseous compounds representative of usual exhaust gas composition from vehicle engines and stationary sources (a) and of various hydrocarbons compounds and water (b).

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.