

Preparation and characterization of inexpensive heterogeneous catalysts for air pollution control: Two case studies

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Abstract

Relatively inexpensive heterogeneous catalysts for two reactions of great importance in air pollution control, NO reduction and VOC combustion, were prepared and characterized. Apart from their common practical goal and the frequent need for simultaneous removal of air pollutants, these reactions share a similar redox mechanism, in which the formulation of more effective catalysts requires an enhancement of oxygen transfer.

For NO reduction, supported catalysts were prepared by adding a metal (Cu, Co, K) using ion exchange (IE) and incipient wetness impregnation (IWI) to chars obtained from pyrolysis of a subbituminous coal. The effects of pyrolysis temperature, between 550 and 1000 °C, on selected catalyst characteristics (e.g., BET surface area, XRD spectrum, support reactivity in O₂) are reported. For IE catalysts, the surface area increased in the presence of the metals while the opposite occurred for IWI catalysts. For the Co-IE catalysts, the highest surface area was obtained at 700 °C. The XRD results showed that, except for Cu (which exhibited sharp Cu⁰ peaks), the catalysts may be highly dispersed (or amorphous) on the carbon surface. For the C–O₂ reaction the order of (re)activity was K ≫ Co > Cu for IE catalysts and K > Cu > Co for IWI catalysts. For NO reduction the orders were K > Co > Cu (IE catalysts) and Cu > Co > K (IWI catalysts). In all cases the catalytic (re)activity for NO reduction was lower than that exhibited for the C–O₂ reaction. The K-IE and Cu-IWI catalysts appeared to be the most promising ones, although further improvements in catalytic activity will be desirable. Some surprising results regarding CO and CO₂ selectivity are also reported, especially for Co catalysts.

In VOC combustion, the effect of the nature of ion B (Fe and Ni) on the partial substitution of ion A (Ca for La) in ABO₃ perovskites (e.g., LaFeO₃ and LaNiO₃) and on their catalytic activity was studied. The perovskite-type oxides were characterized by means of surface area measurements, XRD, temperature-programmed desorption (TPD) and temperature-programmed reduction (TPR). The effect of partial substitution of La³⁺ by Ca²⁺ was more significant for the La_{1-x}Ca_xFeO₃ perovskites. In this case, the electronic perturbation is compensated by an oxidation state increase of part of Fe³⁺ to Fe⁴⁺. The TPD results revealed that, at higher substitution levels, oxygen vacancies are also formed to preserve electroneutrality. For the La_{1-x}Ca_xNiO₃ perovskites, the characterization results showed no evidence of large differences in electronic properties as calcium substitution increases. The La_{1-x}Ca_xNiO₃ perovskites exhibited lower activity than the simple LaNiO₃ perovskite, whereas for the La_{1-x}Ca_xFeO₃ substituted perovskites the most active catalyst (exhibiting the lowest ignition temperature) was obtained at the highest substitution level, La_{0.6}Ca_{0.4}FeO₃.

The performance of both groups of catalysts is briefly discussed in terms of redox processes, in which the interplay between oxygen transfer and electron transfer requires further elucidation for the improvement of catalytic activity.

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1. Introduction

Air pollution control is a pressing need in both industrialized and developing nations. The introduction of effective catalytic processes for pollutant destruction is often hampered in developing nations by excessive emphasis on economic

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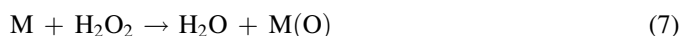
development, at the expense of environmental protection. The affordability of any newly developed catalyst or catalytic process is thus a critical issue, which we have addressed in the following manner: (a) use of coal instead of activated carbon as a precursor for carbon-supported catalysts for NO_x control; (b) use of perovskites prepared from metal nitrates instead of supported noble metals for destruction of volatile organic compounds (VOC).

Carbon has been a popular catalyst support for many years [1]. In some liquid-phase applications it is irreplaceable, because of its tolerance of both highly acidic and highly basic solutions. And yet the virtues and the flexibility of carbon supports have not been exploited to their fullest extent, mostly because of a lack of appreciation of the potentially widely varying surface chemistry of carbon materials [1,2]. Another challenge is related to the ease of reproducible preparation and the cost of carbon-supported catalysts. We have recently initiated a research program that is meant to address both these issues, using inexpensive and abundant coal and biomass as precursors to carbon supports for several representative catalysts: potassium, copper and cobalt. As test reactions we selected H₂O₂ decomposition and NO reduction or decomposition, in which carbon can best exhibit its remarkable flexibility, not only as a support but also as a catalyst in its own right as well as a reducing agent. In addition to the practical importance of each one of these two reactions – the former is a key electron transfer step for the efficient use of batteries and fuel cells [3] and the latter is the key to effectively combating smog and acid rain – they are expected to share a crucial mechanistic feature, as summarized in the following reaction sequence:



The reduction of NO (reactions (1), (3) and (5)) on the free carbon active sites (C_f) is known to follow the same general (“oxygen transfer”) mechanism as both catalyzed and uncatalyzed carbon combustion or gasification [4]: the reactive intermediate (C(O)) is either in (temporary) equilibrium with the stable complex (C–O) or decomposes to CO₂ (at relatively low temperature, e.g., <500 °C; at higher temperatures CO is produced as well). In the often more desirable decomposition of NO (reactions (1), (3) and (4)), carbon acts as a true catalyst, and not also as a reducing agent. This is also a unique feature of H₂O₂ decomposition (reactions (2) and (4)). The proposed mechanism highlights the critical importance of the surface chemistry of carbon, which in turn depends on both its pyrolysis (or heat treatment) conditions and the nature of its precursor [5,6]: the relative abundance of C(O) versus C–O surface species (e.g., at the edges of carbon crystallites and within the graphene layers, respectively) is expected to govern both

carbon (re)activity and product selectivity. In the presence of an active metal catalyst (M) on the carbon support [5,7], the complementary reactions are the more effective adsorption of oxygen from NO or H₂O₂,



and the transfer (‘spillover’) of surface oxygen from the catalyst to the support:



In this communication we present our initial results on the preparation and characterization of such catalysts and compare the performance of catalysts prepared by ion exchange (IE) and those prepared by incipient wetness impregnation (IWI). In particular, our objective is to search for ways to enhance and control the surface migration of adsorbed oxygen; if and when achieved, this could lead to surface oxygen recombination to O₂ rather than overwhelmingly to CO₂ or CO.

From a mechanistic standpoint, combustion of VOCs catalyzed by metal oxides is of interest because analogous oxygen transfer occurs, in this case in the reverse direction: from the solid catalyst to the gas phase. Furthermore, metal oxides for controlling atmospheric pollution control have received wide attention as alternatives to supported noble metal catalysts [8], particularly hexa-aluminate and perovskite-type compounds [9,10], which have even been incorporated into the design of novel combustors [11]. Simple perovskites with the basic formula ABO₃ have been investigated extensively [12,13] for several reasons: (i) transition metal ion contribution of unusual oxidation states; (ii) the amount of non-stoichiometric oxygen; and (iii) the effect of lattice defect structures [14] on catalytic activity. In ABO₃ structures, A is a large cation and B is a small cation of the d-transition series. These oxides consist of close-packed, ordered AO₃ layers which are stacked one on top of the other and the B cations occupy all the interlayer oxygen octahedra. The stacking of an AO₃ layer in the structure may be cubic or hexagonal with respect to its two adjacent layers. The ideal structure of the perovskite-type oxide is of the cubic type [15]. When some distortions of the cubic phase are present, the cation size mismatch and cation or anion non-stoichiometry is induced. For these highly oxidative systems it is of interest to relate bulk and surface defect chemistry to catalytic activity [16].

2. Experimental

2.1. Catalyst preparation

Coal demineralization. A low-rank coal (Pecket, from southern Chile) was used as the carbon precursor. The results of its proximate analysis are listed in Table 1. The as-received particulate coal (AR-C) was ground and sieved to 53–180 μm. The size-graded coal was demineralized using the following protocol: ca. 30 g of AR-C and 200 mL of 5N HCl was magnetically stirred at 55–65 °C for 1 h and filtered. The

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