Conf-950561--1

PNL-SA-24794

STRUCTURE SENSITIVE SELECTIVITY OF THE NO-CO REACTION OVER RHODIUM SINGLE CRYSTAL CATALYSTS

C. H. F. Peden
D. N. Belton[a]
S. J. Schmieg[a]

May 1995

Presented at the
First World Congress In Environmental Catalysts
Conference
May 1-5, 1995
Pisa, Italy

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

(a) General Motors Research & Development Center, Warren, Michigan

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

STRUCTURE SENSITIVE SELECTIVITY OF THE NO-CO REACTION OVER RHODIUM SINGLE CRYSTAL CATALYSTS

Charles H. F. Peden[1], David N. Belton[2] and Steven J. Schmieg[2]
[1]*Pacific Northwest Laboratory*, M.S. K2-12, Richland, Washington 99352 (USA)*
[2]*General Motors Research and Development Center, Warren, Michigan 48090-9055 (USA)*
e-mail: CH_PEDEN@PNL.GOV DBELTON@CMSA.GMR.COM

A Rh(110) single crystal catalyst was found to be much *less* selective for the undesirable N_2O product from the NO-CO reaction than the smooth, close-packed Rh(111) surface suggesting that smaller particle Rh catalysts will be optimum for the production of environmentally benign N_2.

Introduction

The control of automotive emissions of nitrogen oxides (NO_x) in passenger cars is accomplished by a heavy reliance on after-treatment of the engine exhaust using catalytic converters that contain a mixture of platinum (Pt), rhodium (Rh), and sometimes palladium (Pd) [1,2]. Both Pt and Rh are very effective at oxidizing CO to CO_2, but it is generally believed that Pt and Pd are superior for hydrocarbon (HC) oxidation with Rh being best for NO reduction. In the U.S., new government regulations have recently taken effect that mandate substantially reduced NO_x emissions from passenger cars, requiring that they fall from their pre-1994 levels of 1.0 gram/mile to as low as 0.2 grams/mile [2,3]. The current generation of emission control technology already removes over 80% of the NO_x from the exhaust stream under warmed-up conditions, while the new 0.2 grams/mile standard will require improving this efficiency to over 95%. These tougher U. S. standards will take effect at the same time that most European countries are adopting regulations which will effectively double the number of vehicles world-wide that are equipped with a catalytic converter. Given these strong pressures on noble metal supply, it is imperative that Rh and Pt are utilized as effectively as possible for the control of automotive emissions; one part of our effort is focused on obtaining a more detailed understanding of the reactivity of these vital catalyst components. To this end we have a continuing program to define and understand the reaction kinetics over single crystal catalysts under conditions of temperature and pressure comparable to those encountered in automotive exhaust. Because single crystals have well-defined surface structures, surface areas, and no support effects, they are ideal for activity comparisons between metal surfaces with varying geometric structures.

In this paper we examine the effect of surface structure on the NO-CO activity and selectivity by comparing the reactivity of Rh(110) and Rh(111) single crystal catalysts. Selectivity for the two possible nitrogen containing products from NO reduction, N_2O and N_2, is particularly interesting. Here we report that the selectivity of the NO-CO reaction is quite sensitive to the structure of the Rh catalyst metal surface. (A more complete description of these studies will be published elsewhere [4].) The more open Rh(110) surface tends to make significantly less N_2O than Rh(111) under virtually all conditions that we probed with these experiments. Furthermore, under the conditions used in this study, the NO-CO activity over Rh(110), as measured by the rate of NO loss, is somewhat faster than over Rh(111) with a lower apparent activation energy (E_a), 27.6 vs. 35.4

*Pacific Northwest Laboratory is a multiprogram national laboratory operated for the U.S. Dept. of Energy by Battelle Memorial Institute under contract number DE-AC06-76RLO 1830.

kcal/mol. We attribute these results to the greater tendancy of the more open (110) surface to dissociate NO. Notably, more facile NO dissociation on Rh(110) would lead to greater steady-state concentrations of adsorbed N-atoms; thus, the (110) surface favors N-atom recombination over the surface reaction between adsorbed NO and N-atoms to make N_2O. In support of this, post-reaction surface analysis shows only NO on the Rh(111) surface while the Rh(110) surface contains predominantly N-atoms and much lower concentrations of adsorbed NO. NO dissociation on Rh(110) is more favorable than on Rh(111), in part, because it is less-severely poisoned by high surface concentrations of NO. In addition, the more-open (110) surface may be intrinsically more active for the elementary process of dissociating adsorbed NO.

Experimental

The experiments were performed in a custom built system which couples an ultrahigh vacuum (UHV) analysis chamber to a moderate pressure (<100 torr) reactor. The reactor and analysis chamber are separated with a gate valve. A brief description of the experimental procedure for making catalytic rate measurements is as follows: (1) after isolating the UHV analysis chamber, the reactants were leaked into the reactor; (2) the sample was ramped to the reaction temperature at approximately 15 K/sec and the temperature was held (± 2 K) for a specified time interval; (3) the sample was then cooled to room temperature; and finally, (4) the gases in the reactor were expanded into evacuated gas chromatographic sampling loops for quantitative analysis. The UHV analysis chamber is equipped with a wide array of analytical techniques. For this study we used Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and low energy electron diffraction (LEED). Futher details about the apparatus, experimental procedures, and materials are published elsewhere [4].

Results and Discussion

Under the conditions used in this study, the NO-CO activity, as measured by the rate of NO loss, is between 1.3 and 6.3 times faster over Rh(110) than over Rh(111), and the (110) surface exhibits a somewhat lower apparent activation energy (E_a), 27.2 vs. 34.8 kcal/mol, than does the (111) surface. A direct comparison of overall NO-CO reaction rates is made in Figure 1 where the rates of NO consumption obtained on both Rh(110) and Rh(111) are plotted. NO consumption represents the best relative measure of overall activity because it does not depend on the selectivity of the reaction as illustrated in eq. 1.

$$(1+x)CO + 2NO \longrightarrow xN_2 + (1-x)N_2O + (1+x)CO_2 \qquad (0 \le x \le 1) \qquad (1)$$

Although the turnover numbers for NO reaction can be quite similar on the two different surfaces, we find large differences between Rh(110) and Rh(111) with regard to their selectivities for the two competitive nitrogen-containing products, N_2O vs. N_2. The more open Rh(110) surface tends to make significantly less N_2O than Rh(111) under virtually all conditions that we probed with these experiments. An example of these results is illustrated in Figure 2 showing the N_2O selectivity, $S^{N_2O} \equiv$ [mol N_2O]/[mol N_2O + mol N_2], as a function of NO partial pressure at a constant CO pressure of 8 Torr on the two single crystal surfaces studied by us. For Rh(111) at 623 K, we observe no change in S^{N_2O} (≈80%) even for the lowest NO pressure of 1 Torr. Figure 2 also shows that there is a considerable difference in the N_2O selectivity on Rh(110) at all NO pressures. Furthermore, we observe a marked decrease in the N_2O selectivity on Rh(110) at NO partial pressures below about 10 Torr for a reaction temperature of 623 K.

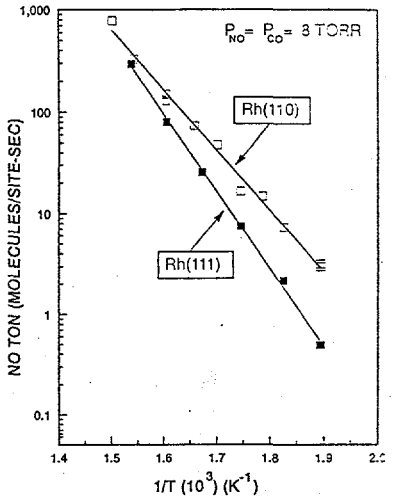

Fig. 1 Rate of NO loss over Rh(110) and Rh(111).

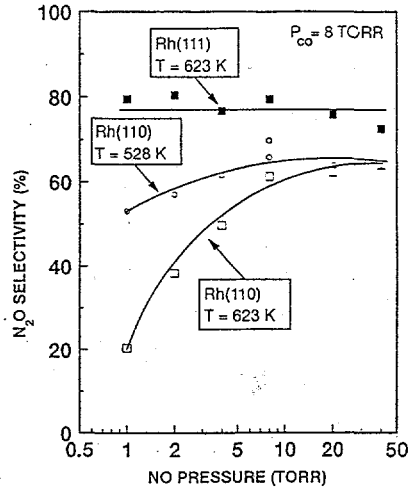

Fig. 2 N_2O selectivity plotted as a function of NO partial pressure.

In a recent paper [5], it was concluded that N_2O selectivity on Rh is a strong function of NO surface coverages during reaction. Therefore, it was reasonable to assume that the different selectivities we observed on Rh(110) and Rh(111) might be a direct result of differing steady-state concentrations of adsorbed surface species (notably NO) during reaction. One way to indirectly assess the state of the reactive surface is to perform a UHV surface spectroscopic measurement *ex-situ* after reaction. In this case, we chose x-ray photoelectron spectroscopy (XPS) because it can clearly distinguish between adsorbed nitrogen present as either molecular NO or as N-atoms formed by NO dissociation during reaction. Figure 3 shows the N(1s) region of XPS spectra taken after NO-CO reaction over both Rh(110) and Rh(111) at 528 K, and NO and CO partial pressures of 8 torr each. After the reactions were run, the samples were cooled in the reactant gases, freezing out the reaction, then the reactor was evacuated and the samples transferred to the UHV chamber for XPS analysis. For Rh(111), the spectrum shows only a single N(1s) feature with a binding energy near 400.3 eV due to adsorbed NO. In contrast, the NO N(1s) feature on Rh(110), while present, is significantly smaller than another N(1s) feature at lower binding energy, 397.6 eV, due to adsorbed N-atoms.

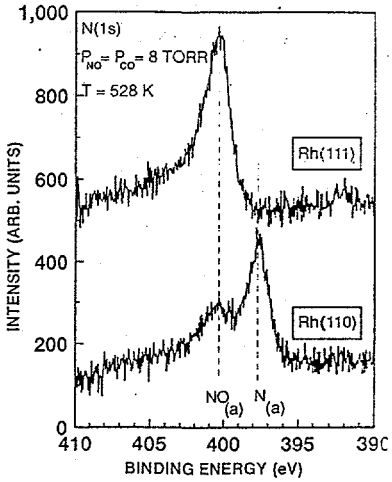

Fig. 3 N(1s) XPS spectra obtained after NO-CO reaction at 500 K in 8 torr of each reactant.

The kinetic results that we obtained on both Rh surfaces (more completely described elsewhere [4]) can all be readily accounted for with a model that involves the following elementary steps: CO and NO molecular adsorption equilibria to form CO(ad) and NO(ad); NO(ad) dissociation to adsorbed N- [N(ad)] and O-atoms [O(ad)]; CO(ad) + O(ad) reaction to give CO_2(g); N(ad) + N(ad) reaction to give N_2(g); and NO(ad) + N(ad) reaction to give N_2O(g). In rationalizing the kinetic data within this model [4], it is critical to make the assumption that NO dissociation is the important step (probably rate-limiting) under the high-pressure reaction conditions used in these experiments. The mechanistic arguments that we make also rely on the important fact that NO dissociation rates are suppressed at high NO surface coverages. Therefore, we believe that the NO adsorption/desorption equilibrium is a primary determining factor of N_2 and N_2O formation rates and, thus, N_2O selectivities for both Rh(111) and Rh(110) surfaces.

Finally, we consider more completely the possible explanations for the significantly different N_2O selectivities observed over the two Rh single crystal catalysts, and the fact that this selectivity shows quite different sensitivities to NO pressure (Figure 2), reaction temperature [4], and NO conversion [4]. At this point in time our understanding of the rate constants of some elementary steps is too limited to allow us to make definitive statements as to the details of how the surface structure effects the N_2O selectivity. For the following, we assume that different selectivities arise simply from differences in the rates of the two surface reactions that give N-atom containing products therefore not requiring additional elementary steps in the model than those described above. Furthermore in the absence of information concerning N-atom recombination rates and N_2O formation rates on Rh(110), we assume that the *rate constants* for these reactions are similar on the (111) and (110) Rh surfaces. With these assumptions, the differences in N_2O selectivity must arise from different steady-state *coverages* of NO and N-atoms on these two surfaces during high-pressure reaction. In fact, we have some fairly direct evidence in support of this assumption from the XPS results shown in Figure 3. The main question that needs to be addressed is what could give rise to these differences in steady-state surface coverages. It is known that NO dissociation is severely poisoned by high surface concentrations of NO on Rh(111) [5]. Because Rh(110) has a more open surface structure, we believe that adsorbed NO may be less of a poison for NO dissociation on this surface. In addition, the (110) surface may be intrinsically more active for the elementary process of dissociating adsorbed NO.

In summary, the N_2O selectivity differences on Rh(110) and Rh(111) single crystal catalysts we observed in this study are quite dramatic, and the differences can be readily understood in terms of different steady-state coverages on NO and N-atoms on the two surfaces. However, the underlying causes of differing steady-state surface coverages may be quite subtle and can only be understood by making additional detailed measurements of the NO adsorption (including sticking coefficients), desorption and dissociation rates (for example see [6]).

References

1. K.C. Taylor, Chemtech, **20** (1990) 551.
2. K.C. Taylor, Catal. Rev.-Sci. Eng., **35** (1993) 457.
3. J.G. Calvert, J.B. Heywood, R.F. Sawyer, and J.H. Seinfeld, Science **261** (1993) 37.
4. C.H.F. Peden, D.N. Belton, and S. J. Schmeig, J. Catal. (1995) in press.
5. K.Y.S. Ng, D.N. Belton, S.J. Schmieg, and G.B. Fisher, J. Catal. **146** (1994) 406.
6. D.N. Belton, C.L. DiMaggio, and K.Y.S. Ng, J. Catal. **144** (1993) 273.