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The promotional effect of Na for the NO reduction by CO on supported Pt, Pd and Rh catalyst

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The role of Na as a promoter for the NO reduction by CO was investigated on welldispersed Pt, Pd and Rh catalysts supported on γ -Al₂O₃, 8 mol% Y₂O₃ stabilized ZrO₂ (YSZ) and 4 mol% WO₃ doped TiO₂ respectively at temperatures 150°C to 500°C. The choice of the support materials, i.e. γ -Al₂O₃ for Pt, YSZ for Pd and WO₃-doped-TiO₂ for Rh was dictated by a recent kinetic study which showed that these supports maximize the turnover frequency of the CO+NO reaction on these three metals, respectively. Significant promotional effects of Na were observed in the present study for the well-dispersed supported Pt and Pd catalysts, while the opposite trends were observed on Rh were Na actually decreases the catalytic rate. Thus on Pt/ γ -Al₂O₃ at 425°C a Na content of 0.43wt% enhances NO conversion from 30% to 100%. On Pd/YSZ at 375°C a Na content of 0.03wt% enhances NO conversion from 80% to 100%. On Rh/TiO₂ (4% WO₃) at 275°C, however, a Na content of 0.048wt% causes a decrease in NO conversion from 72% to 8%.

Stability tests of a Na-promoted Pt catalyst at 500°C for up to 50hrs show no deterioration in catalytic rate. This must be due to the formation of stable surface sodium complexes. The promotional action of sodium for the NO+CO reaction on the Pt and Pd catalysts appears to be due to enhanced NO chemisorption and dissociation on these metals while on Rh catalyst NO dissociation is already pronounced. The present results may be useful in the design of three-way catalytic converters as they could allow, in principle, for significant substitution of Rh by Pt and Pd metals.

1. INTRODUCTION

The catalytic reduction of NO by CO is of major environmental importance with respect to the removal of toxic emissions from both stationary and automotive sources [1, 2]. Platinum group metals are used widely for the catalytic removal of NO from effluent gases. Because of its superior ability to dissociatively chemisorb NO [1], Rh is the preferred catalyst for NO reduction and thus the key metal constitute in three-way catalysts (TWCs) for the same reaction. On the other hand, due to its scarcity and high cost, a Rh substitution in catalytic converters, by

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Pt and Pd noble metals would be desirable.

Promoters play a key role in industrial heterogeneous catalysis, since their addition modify the intrinsic metal surface chemistry with respect to activity and/or selectivity [3]. Although alkali metals exhibit a strong promotional effect for NO dissociation on transition metal surfaces [3], very few studies on the effects of alkali promotion have been carried out. Recently, it was found that sodium, which can form surface carbonates and surface Na-CO complexes under reaction conditions [4, 5] has a strong promotional effect for the CO+NO reaction [6]. It significantly enhances both the rate of NO reduction and the product selectivity to N₂ by enhancing the surface dissociation of NO [4, 5]. In the present work we demonstrate high enhancements in activity of Na promoted Pt and Pd supported catalysts during NO reduction by CO. The opposite trends were observed on Rh catalysts, where Na actually decreases the catalytic rate.

Pt, Pd and Rh catalysts were supported on γ -Al₂O₃, 8 mol% Y₂O₃ stabilized ZrO₂ (YSZ) and W⁶⁺-doped TiO₂ respectively, since it was found [7] that these support materials maximize turnover frequency of the CO+NO reaction on these three metals.

2. EXPERIMENTAL

Pd, Pt and Rh catalysts were prepared by impregnation of the supports with a low PH (1-3) solution of PdCl₂, H₂PtCl₆, RhCl (Alfa Products) respectively to yield 0.5 wt% metal loadings. The following powder supports were used: ZrO₂ (8 mol% Y₂O₃) (Zirconia Sales), γ -Al₂O₃ (Alfa Products) and W⁶⁺ doped TiO₂ (Degussa P25). The later support was prepared by thermal treatment of TiO₂ and WO₃ (Alfa Products) at 900°C for 5h. Sodium was added to the catalysts by impregnation with a NaNO₃ solution followed by drying and calcining at 400°C.

Before any measurement, the catalysts were reduced in a quartz tube by He flow at 250° C for 1h followed by H₂ flow at 400°C for 1h. Kinetic studies were carried out in a CSTR-type reactor. The NO reduction by CO was studied at temperatures 150° C to 500° C. Analysis of reactants and products was carried out by on line gas chromatography and chemiluminescence analysis. N₂, N₂O, CO, CO₂ were measured via GC, while NO was continuously monitored via the chemiluminescence analyser.

Reactants were L'Air Liquide certified standards of 1%NO and 10% CO in He. There were further diluted in ultrapure He (99.999%) at atmospheric total pressure. The total flow rate of the reactant gas mixture was kept constant for all experiments at 200 cm³ STP/min, and the partial pressures of P_{NO} and P_{CO} at 0.5 kPa. In all runs 50 mg of catalyst material were used.

3. RESULTS AND DISCUSSION

The present results show a significant effect of sodium on the catalyst activity of Pt, Pd and Rh. The degree of this influence is strongly dependent on the metal and on the amount of

sodium added.

3.1 Pt-based catalysts

Fig. 1a depicts the effect of temperature and sodium addition on the NO conversion of the Pt-catalysed NO reduction by CO at constant partial pressures of NO and CO.



Figure 1. Effect of catalyst temperature and sodium content on the NO conversion (a) and effect of Na content on the NO conversion at T= 425^{9} C (b) during the NO+CO reaction.Catalyst: 0.5wt%Pt/ γ -Al₂O₃; Conditions:P_{CO}=0.5kPa, P_{NO}=0.5kPa.

It can be seen that catalysts which contain a significant amount of sodium (0.43, 0.86 wt% Na) show an important shift of their light off temperature to much lower values, compared to the catalyst which is free of sodium or to those containing a small amount of sodium. Thus, in the case of 0.43 wt% Na catalyst the light off temperature is 363° C while the light off temperature of the 0 wt% Na catalyst is 427°C.

These results are also presented in Fig. 1b which shows the dependence of sodium content of the catalyst on the NO conversion at a constant temperature of 425°C. Thus, a sodium content of 0.43 wt% enhances NO conversion from 30% to 100%. Similarly a Na content of 0.86 wt% enhances NO conversion from 30% to 95%.

Similar results have been obtained in the recent Electrochemical Promotion studies of the CO+NO reaction on thin Pt-films deposited on β "-Al₂O₃ which is a Na⁺ conductor [4, 6,8]. These studies showed that sodium has a strong promotional effect for the CO+NO reaction. It significantly enhance both the rate of NO reduction and the product selectivity to N₂ by enhancing the surface dissociation of NO.

The stability of Na promoted catalysts was tested at 500°C for up to 50h on stream. No

measurable deterioration in catalytic performance was observed. This must be due to the formation of stable surface sodium complexes and compounds, which stabilize Na on the surface [6,8].

The thermal ageing resistance of sodium promoted catalysts was also studied. A Na contamined (0.43wt%) Pt catalyst and a Na-free Pt catalyst were preatreated at 700°C for 3hrs. Fig.2 shows the temperature dependence of the NO conversion of the catalysts before and after the thermal treatment. It is obvious that both the Na-promoted and the Na-free catalysts have lost surface area but the light-off temperature of the Na-promoted catalyst remains higher.



Figure 2. Effect of catalyst temperature on NO conversion for a Na-free (cycles) and a 0.43wt% Na-content (triangles) catalyst, before (open symboles) and after (closed symboles) a thermal ageing at 700°C for 3hrs. Conditions: $P_{CO} = 0.5 \text{ kP a}$, $P_{NO} = 0.5 \text{ kP a}$,

For example at 425°C the catalytic activity was reduced up to 40% for the Na-promoted Pt catalyst and up to 11% for the Pt catalyst. The sintered Na contamined catalyst exhibits a performance similar to the Pt catalyst before the thermal treatment. It is clear that although there is a notable decrease in catalytic activation due to sintering. Na-promoted Pt catalyst presents a better performance than Na-free Pt catalyst.

3.2 Pd-based catalysts

Similarly to the case of Pt catalysts sodium was found to enhance the performance of the Pd catalysts. The effect is, however, smaller as shown in Fig. 2. Thus, the light off temperature of 0.03 wt% Na promoted Pd catalyst is 320°C, while the light off temperature of 0 wt% Na catalyst is 338°C.

Fig. 3b shows the effect of sodium content of the catalyst on the NO conversion at 375° C. Over a large range of sodium content (0.007-0.16 wt%), sodium promotes the catalytic activity. Thus a Na content of 0.03 wt% enhances NO conversion from 80% to 100%, while a Na content of 0.078 wt% enhances NO conversion from 90% to 100%. These can be rationidized in terms of Na-induced dissociation of chemisorbed molecular NO, which is thought to be the reaction initialing step [4,6,8].



Figure 3. Effect of catalyst temperature and sodium content on the NO conversion (a) and effect of Na content on the NO conversion at T= 375° C (b) during NO+CO reaction.Catalyst: 0.5wt%Pd/YSZ; Conditions:P_{CO}=0.5kPa, P_{NO}=0.5kPa.

3.3 Rh-based catalysts

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In the case of Rh catalysts, sodium tends to suppress the catalytic activity. Fig. 4a illustrates the effect of temperature on the NO conversion. It can be observed that sodium addition causes an increase in light off temperature.



Figure 4. Effect of catalyst temperature and sodium content on the NO conversion (a) and effect of Na content on the NO conversion at T= 275^{9} C (b) during NO+CO reaction.Catalyst: 0.5wt%Rh/TiO₂(W⁶⁺); Conditions:P_{CO}=0.5kPa, P_{NO}=0.5kPa.

Thus a 0.0097 wt% Na-Rh catalyst has a light off temperature of 270°C, while the light off temperature of Na-free catalyst is 263°C. The adverse effect of sodium on Rh catalysts is shown better in Fig. 4b which illustrates the dependence of sodium content on NO conversion at 275°C. Thus a sodium content of 0.048 wt% causes a pronounced decrease in NO conversion from 72% to 8%.

It is known [1,2] that Rh promotes NO dissociation on its surface. Thus any further increase of the strength of chemisorptive bond of N and O adatoms due to sodium addition, is expected to decrease the rate as experimentally observed.

The selectivity to N_2 , was also found to vary between 45-70%, 20-30% and 20-40% for Pt, Pd and Rh respectively with varying Na content, but the analysis was not detailed enough and this point is currently under investigation.

CONCLUSIONS

In the present study that Na addition significantly affects the performance of Pt/Al_2O_3 , Pd/YSZ and Rh/TiO_2 catalysts for the NO reduction by CO. In the case of Pt-based catalysts Na has a strong promotional effect. Enhancement of the catalytic rate by up to 70% were obtained. Similar promotional effects due to sodium were observed with the Pd-based catalysts. The catalytic activity was increased by a factor of 20%. However in the case of Rh-based catalysts, the opposite behaviour was observed. Sodium poisons the catalyst and decreases its activity by a factor of 60%.

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Ethanol oxidation on Three-way automotive catalysts. Influence of Pt-Rh interaction.

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Abstract

Ethanol oxidation was studied under lean conditions on platinum/alumina catalysts modified by rhodium and/or lanthanum oxide. The results on alumima support suggest that the formation of bimetallic Pt-Rh particles enhances the production of acetaldehyde, particulary after oxidizing thermal aging of the Pt-Rh/alumina catalyst prepared by coimpregnation. The addition of lanthanum oxide to alumina allows to avoid the formation of Pt-Rh alloy after high temperature treatment and therefore induces a decrease of the production of acetaldehyde.

1. Introduction

The clean Air Act amendements of 1990 requires increased use of oxygenated compounds such as alcohols and ethers in motor fuels. Oxygenates in gasoline reduce vehicle emissions and act as high-octane replacements for harmful components that must be removed from reformulated fuels. In areas where air quality problems are severe, there is interest in using pure oxygenate fuels such as methanol or ethanol. But the use of ethanol-fueled passager cars produces high emissions of aldehydes relative to gasoline fueled cars, which lead to the formation of photochemical smog. Moreover, upon installation of three-way Pt-Rh catalysts and after approximately 5,000 km use, acetaldehyde emissions increased beyond the levels observed without catalyst (1).

The present work deals with ethanol oxidation which was performed in a flow reactor under lean conditions. Catalysts were evaluated by studying their ligh-off behaviour and by determining the amount of acetaldehyde produced during the temperature programmed experiment from ambient temperature to 500°C.

2. Experimental

2.1 Catalyst preparation

The supports used were a γ -Al₂O₃ with a BET area of 100 m²/g and the same alumina modified by addition of lanthanum acetate in order to obtain an Al₂O₃-La₂O₃ support with 12 wt % lanthanum oxide after calcination at 500°C. Monometallic catalysts were prepared by coimpregnation of chloroplatinic acid or rhodium trichloride.