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Catalysis by Single Ions in a Host Lattice

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Abstract Heterogeneous catalytic reactions are commonly occurring on the surface of a finely dispersed catalyst. Here, evidence is presented that platinum on a gadolinium doped ceria matrix is present as individual Pt^{2+} ions, which catalyze the partial oxidation of hydrocarbon molecules. Similarly, ruthenium substituted on the "B" site of $LaCrO_3$ is shown to oscillate between the plus three and zero oxidation states when exposed to a flowing stream of hydrocarbons, steam and air. In both cases, single hetero ions in a host lattice facilitate the catalytic reaction.

Keywords Single ion catalysis · Platinum ions · Ruthenium ions · Perovskites · Fuel reforming · GDC · $LaCrO_3$

1 Introduction

Heterogeneous catalysts typically consist of finely dispersed metals on an oxide substrate. An exception was reported by Flytzani-Stephanopolous [1] and coworkers. They showed that single gold or platinum ions were catalyzing the water gas shift reaction. Here, we made similar observations for the reforming of hydrocarbons into hydrogen-rich gas by individual metal ions with two different types of catalysts. Initially, platinum supported on gadolinium doped ceria catalyst was used, and as shown below, all of the platinum in the freshly prepared catalyst was found to be in the Pt^{++} state and not as platinum metal. This catalyst was substantially more active than platinum on alumina where the platinum is present as metal grains. To test the concept whether noble metal ions were facilitating the reforming of the hydrocarbons, a totally different class of materials was prepared and evaluated. Ruthenium was substituted for a small amount of the "B" site element in several perovskites. More specifically, when 5% of the chromium in $LaCrO_3$ is replaced with ruthenium, the substituted material is much more active than the undoped lanthanum chromite. Although the ruthenium was firmly anchored in the perovskite lattice as individual Ru^{+++} ions, it promoted the reforming reaction.

The generalized reaction that was catalyzed is shown in Eq. 1. Hydrocarbons ranging from methane to iso-octane, but also multi-cyclic and aromatic hydrocarbons were converted to hydrogen-rich mixtures by partial oxidation in the presence of water. This reaction is also referred to as auto-thermal reforming and is a good route for making hydrogen for fuel cells [2]

$$C_nH_m + xn(O_2 + 3.7N_2) + nH_2O \rightarrow (1-2x)nCO + 2xnCO_2 + (m/2+n)\,H_2 \quad (1)$$

In this reaction, x refers to the O_2/C ratio. The oxygen to carbon ratio affects the adiabatic reaction temperature [2] and is chosen to establish temperatures in the 600–800 °C

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range. The steam to carbon ratio can also be independently varied. It influences the hydrogen concentration, and more importantly whether carbon precipitates. In this work the O_2/C ratio is typically 0.4 and the H_2O/C ratio is usually 1.

Here, we discuss some representative catalytic activities, but are mainly concerned with the reaction mechanism.

2 Experimental

Other than Pt/Al_2O_3 which was acquired from the commercial source (Sigma-Aldrich), other catalysts or catalyst support were made in-house by combustion synthesis [3]. For CGO, a known quantity of cerium nitrate is dissolved in water together with 20 mol% gadolinium nitrate and 0.5 wt.% of hexachloroplaticic acid. Glycine is added in a 5:9 molar ratio to the sum of ceria and gadolinia. The solution is slowly boiled down to dryness in a glass beaker. Upon further heating, combustion occurs, yielding a very fine, uniform powder. The perovskite catalyst was prepared similarly from a nitrate solution of lanthanum, chromium and ruthenium. All the catalysts by combustion method were prepared in a single step. No post addition of metal was used.

The activity of the catalysts was characterized in an apparatus shown in Fig 1. A powder sample of about 1/2 g was exposed to the hydrocarbon/air/steam mixture as shown schematically in Fig. 1. Gas compositions were analyzed by gas chromatography (HP 5890) after the steam was removed by the condenser and drying column or with a quadrupole mass analyzer. In addition to the major components such as H_2, CO, CO_2, N_2, etc., trace hydrocarbons in the reformate such as CH_4, C_2H_2, C_2H_4, etc., were also measured quantitatively.

Temperature programmed reactions were obtained using an Altamira instrument with isobutane and O_2/C ratio of 0.5 and H_2O/C ratio of 0.9. The temperature was raised at 2 °C per minute.

XPS spectra were obtained with a Surface Science SSX-100 X-ray photoelectron spectrometer. XANES and EXAFS were obtained through the experiments at the Sector 10 of Advanced Photon Source at Argonne.

3 Results and Discussion

Figure 2 shows the composition of the reformate of isooctane over the platinum in CGO catalyst at 800 °C for

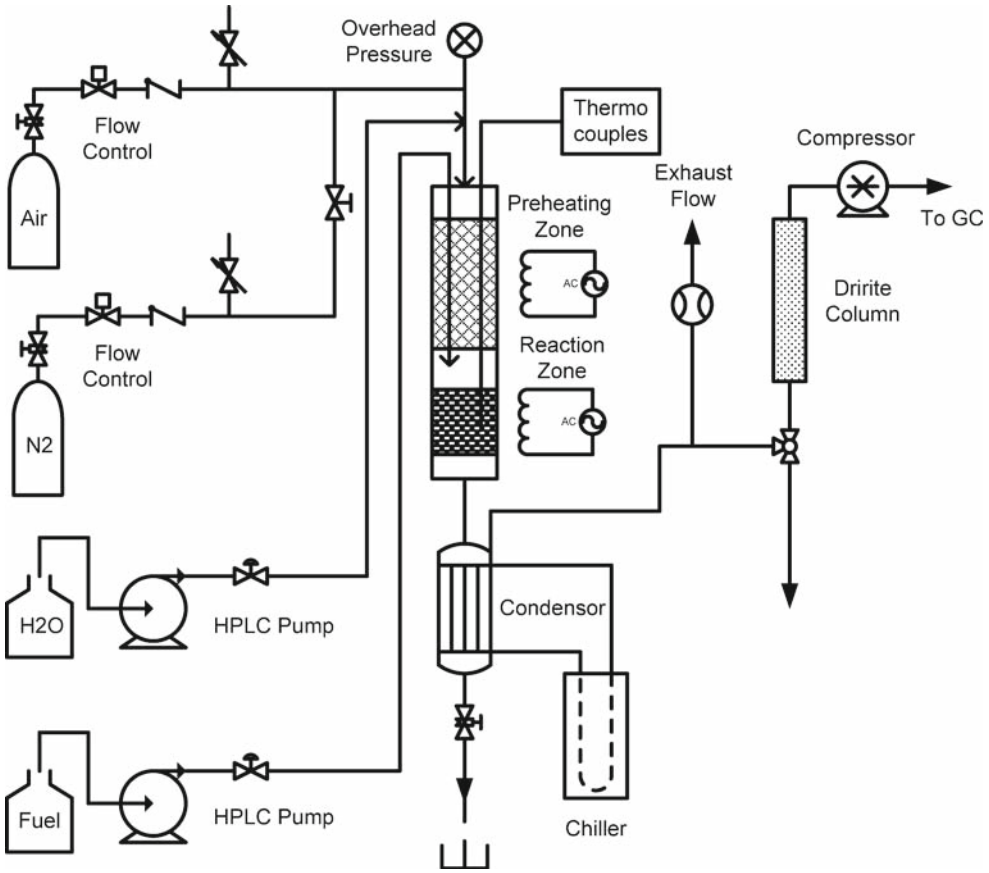

Fig. 1 Schematic of the test apparatus

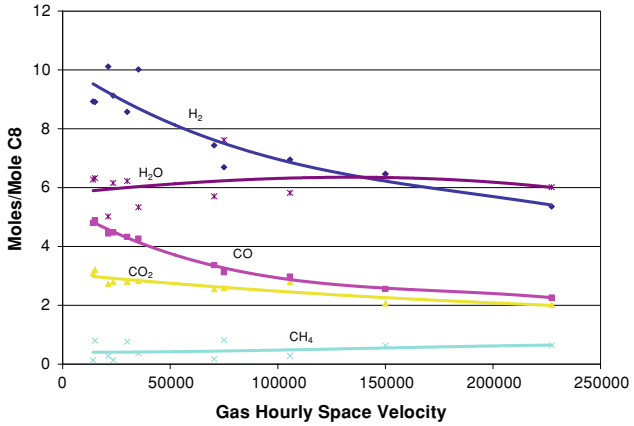

Fig. 2 Product composition of reformed iso-octane at 800 °C

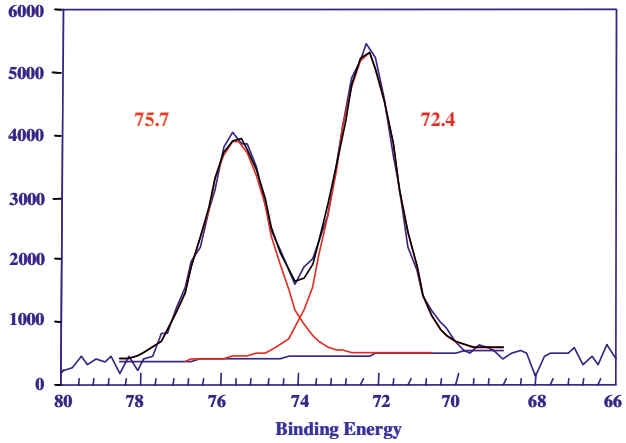

Fig. 4 XPS spectrum of platinum on CGO showing characteristic binding energies of Pt^{2+}

space velocities ranging from 10,000 to 225,000 h^{-1}. At the lowest space velocities the hydrogen yield is about 9.5 moles of hydrogen per mole of iso-octane, which is close to the thermodynamic equilibrium. The fuel conversion was 98% up to 100,000 h^{-1} and decreased some thereafter. At higher space velocities, hydrogen and CO yields decreased, but the methane content went up slightly suggesting that the steam reforming reaction does not reach equilibrium at the higher space velocities.

Figure 3 shows temperature programmed oxidations of iso-butane over Pt/CGO and Pt/Al_2O_3 catalysts. On both catalysts oxygen is completely consumed between 150 and 200 °C, reacting with iso-butane to yield steam and carbon dioxide. Hydrogen and CO begin to form at 500 °C as the remaining iso-butane, steam and carbon dioxide begin to disappear. This indicates that steam reforming and apparently CO_2 reforming are the source for the hydrogen.

It is also readily apparent that Pt/CGO is a more active catalyst than platinum on alumina. A TPO run over CGO without any platinum did not yield any hydrogen until 700 °C was reached.

Attempts were made to determine the size of the platinum particles on CGO by high resolution scanning electron microscopy (SEM), surprisingly, no platinum particles were detected. Close, examination of Pt/CGO catalyst by XPS and XANES found that platinum actually exists in the oxidized state. For example, the XPS spectrum in Fig. 4 shows that the platinum on the surface of the CGO was in the Pt^{++} state and not as metal.

Further, comparative study of EXAFS spectra for the same platinum on CGO and of platinum on undoped ceria confirmed that there were no platinum-platinum bonds, only Pt–O–Ce in Pt/CGO. On the other hand, tiny Pt_4 clusters were observed for platinum on undoped ceria. The results are summarized in Table 1.

To explain these results, we need to recall that gadolinium doped ceria is an excellent oxide ion conductor with a high concentration of oxide ion vacancies on the surface [4]. Apparently platinum metal can dissolve into the surface of the GDC as shown in Eq. 2

$$Pt + V_o^{\cdot\cdot} + 1/2\ O_2 \leftrightarrow Pt^{2+} + O^{2-} \qquad (2)$$

where $V_o^{\cdot\cdot}$ represents an oxide ion vacancy. Platinum and gold ions in aqueous solutions are known to activate carbon-hydrogen bonds and to oxidize methane to methanol [5, 6, 7]. The exact mechanism for this reaction is not established, but it is believed that the metal ions react with the carbon–hydrogen bond via an oxidative addition,

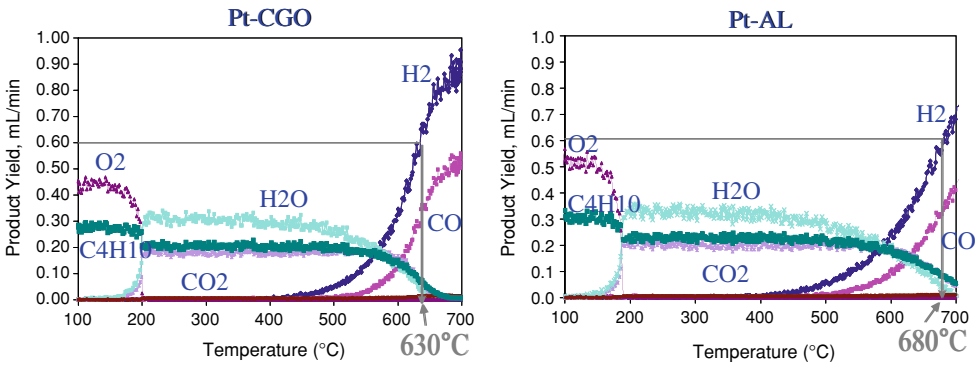

Fig. 3 TPOs of iso-butane over Pt/CGO and Pt/alumina

Table 1 Summary of EXAFS of platinum on ceria

Sample	Particle size (Å)	Comments
Pt/CeO_2	>10	Pt_4
		NO Pt–O
Pt/CGO	<5	Pt–O–Ce
		No Pt–Pt

separating the hydrogen from the carbon. We postulate that the platinum ions in the surface of the ceria oxidize hydrocarbons in a similar manner as shown in Eq. 3, forming hydrogen, carbon monoxide and an oxide ion vacancy. The platinum atoms are then re-oxidized as shown in Eq. 4, completing the steam reforming reaction.

$$CH_4 + Pt^{2+} + O^{2-} \leftrightarrow CO + 2H_2 + Pt + V_o^{\cdot\cdot} \quad (3)$$

$$H_2O + Pt + V_o^{\cdot\cdot} \leftrightarrow Pt^{2+} + O^{2-} + H_2 \quad (4)$$

$$CH_4 + H_2O \leftrightarrow 3\,H_2 + CO$$

To further explore this concept of catalytic oxidation by individual metal ions, an entirely different class of materials was prepared. Perovskites of the general composition ABO_3 can be substituted on the "A" and on the "B" site. Lanthanum chromite, $LaCrO_3$ and lanthanum aluminite, $LaAlO_3$ are particularly stable perovskites that are not reduced in hydrogen. Stability in both hydrogen and oxygen are necessary for reforming catalysts, because in a catalyst bed the gas in the front of the bed is oxidizing but reducing in the back. By substituting 5% of the chromium or aluminum with ruthenium, we anchored a more reducible ion into a stable matrix, analogous to the platinum in ceria.

Figure 5 shows the efficiency from reforming dodecane over several ruthenium substituted lanthanum chromites and an aluminite. The O_2/C ratio was 0.5, the H_2O/C was 2 and the space velocity 100,000 h^{-1}. In this case, dodecane instead of isooctane was used as the surrogate fuel for diesel. Our laboratory study has found that the impacts to the catalytic behavior are similar when the sizes of the alkanes are not substantially different.

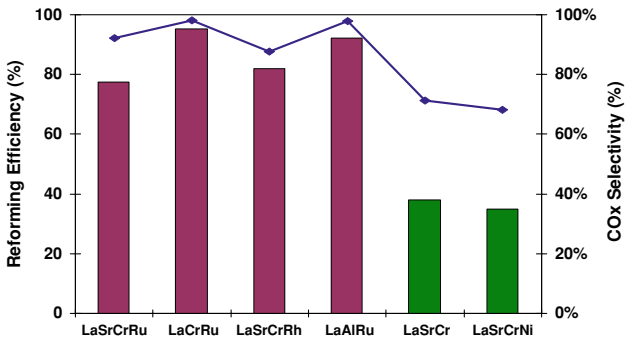

Fig. 5 Reforming efficiencies of ruthenium and rhodium doped perovskites

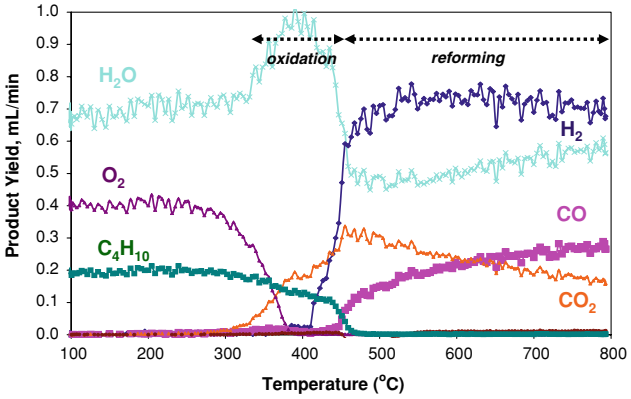

Fig. 6 TPO of iso-butane on ruthenium doped lanthanum chromite

The ruthenium doped chromites and aluminites were clearly much more active for the reforming of dodecane than the undoped material. Strontium substitution on the A site converts the chromite into an electronic conductor, which was expected to be beneficial. It was not.

A temperature programmed reforming of iso-butane on the ruthenium doped chromite catalyst is remarkably similar to the platinum on CGO TPO, as is shown in Fig. 6. Oxygen is completely consumed at lower temperatures before the steam reforming reaction begins at only 380 °C.

XANES and EXAFS of freshly prepared ruthenium doped perovskite and ruthenium(IV) oxide as well as ruthenium(III) acetylacetonate are shown in Fig. 7a and b. In Fig. 7a, LSCR120 and LSCR 80 refer to the perovskite samples that were calcined at 1,200 °C and 800°, respectively. Both XANES spectra are similar to the ruthenium(III) acetate, proving the three valent oxidation state of the ruthenium. In Fig. 7b EXAFS for the same materials are shown in the same order. Integration of the area under the major peaks at a radius of 1.94 A yields a coordination of the ruthenium by six oxygen's in the upper three EXAFS and only 4.7 in the sample calcined at 800 °C. Apparently, the lattice was not fully annealed at the lower calcination temperature, but the data for the sample that was calcined at 1,200 °C are consistent with Ru^{+++} in the octahedral coordination of the perovskite lattice.

The used catalyst was essentially unchanged since lanthanum chromite has been shown to be stable in oxygen and hydrogen as bipolar plate material in solid oxide fuel cells [8]. However, at the exit of the catalyst bed some of the ruthenium was found to be in the zero oxidation state while most is still plus three.

As was postulated for the platinum on doped ceria catalyst, it is apparent that reforming of dodecane is facilitated by ruthenium ions on the surface of the perovskite lattice oscillating between the plus three and zero oxidation states.

To corroborate the redox concept, nickel and rhodium were substituted into the lanthanum chromite lattice

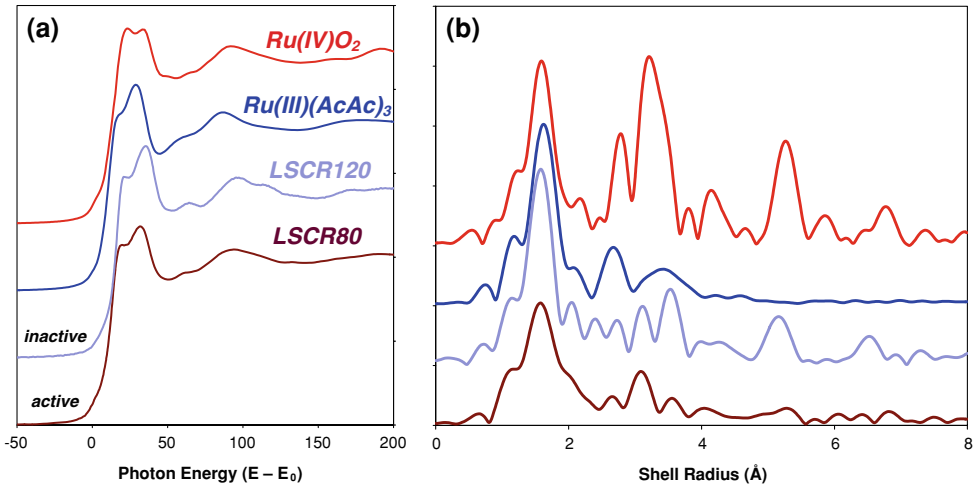

Fig. 7 XANES (**a**) and EXAFS (**b**) of ruthenium doped lanthanum chromite and of reference compounds

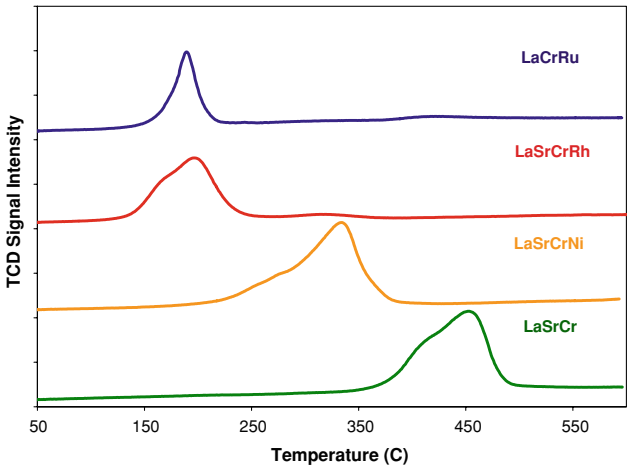

Fig. 8 Temperature programmed reductions of several doped perovskites

analogous to ruthenium. Temperature programmed reductions of ruthenium, rhodium and nickel doped catalyst are shown in Fig. 8 together with undoped chromite. Clearly, ruthenium and rhodium are chemically active while the perovskite host lattice is unaffected.

4 Conclusions

Experimental evidence is presented showing that individual noble metal ions supported in host lattices catalyze the reforming of hydrocarbons. The metal ions oscillate between two different oxidation states and oxidize the hydrocarbon molecules. This finding has perhaps broader implications. Whenever strong metal/support interactions are inferred in the catalysis literature, the surface atoms of a metal catalyst that is supported on oxides may also be in a higher oxidation state and may act as an oxidant.

Ultimately, the surface redox chemistry dictates the catalysis of fuel reforming between the reductants (hydrocarbon fuels) and oxidants (oxygen and water). We should point out, however, that current study addresses only on the mechanism over freshly prepared, virgin catalysts. Through extended catalytic reforming reaction at elevated temperature in the presence of hydrogen rich reformate, the highly dispersed platinum or ruthenium atoms may agglomerate to some extend into metal crystallites. The investigation on the aging behavior of these catalysts will be reported in a separate paper.

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References

1. Fu Q, Saltsburg H, Flytzani-Stephanopoulos M (2003) Science 301:935–938
2. Krumpelt M, Krause TR, Carter JD, Kopasz JP, Ahmed S (2002) Catal Today 22:3–16
3. Chick LA, Bates JL, Pederson LR, Kissinger HE (1990) In: Proceedings of the 1st international symposium on SOFCs, vol 89–11. The Electrochemical Society
4. Scanion PJ, Bink RAM, van Berkel FPF, Christie GM (1998) Solid State Ionics 112(1–2):123
5. Shilov AE, Shulpin GB (1997) Chem Rev 97:2879
6. Sen A (1998) Acc Chem Res 31:550–557
7. Periana RA, Taube JD, Gamble S, Taube H, Satah T, Fuji H (1998) Science 280:560
8. Armstrong TA, Stenvenson JW, Peterson LR, Raney PE (1995) In: Proceedings of the 4th international symposium on solid oxide fuel cells, vol 944. The Electrochem Society