

## THE CATALYTIC DECOMPOSITION OF METHANOL INTO SYNGAS FOR USE AS AN AUTOMOTIVE FUEL

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### ABSTRACT

Although methanol is thought to be an excellent automotive fuel, it has a smaller volumetric fuel value than gasoline. The catalytic decomposition of methanol into syngas, prior to its combustion in the engine, improves its fuel value by approximately 14%. Palladium and platinum on modified alumina supports demonstrate the necessary qualities for this process. The catalytic activity and thermal stability of palladium is strongly affected by the nature of the catalyst support used. A gamma-alumina support was modified with the oxides of Li, Mg, Cs, and La. The effect of the modified support on the activity, selectivity, and thermal stability of the palladium metal was studied during exposure to a thermal cycle of 300, 500, and 300°C. The profound difference in catalyst behavior may be due to strong metal-support interactions, to variations in metal dispersion, or to chemical alteration of the palladium. In order to determine the chemical state of the palladium metal and the modified support before and after testing, the catalysts were characterized by TPD, XRD, XPS, and volumetric chemisorption techniques.

### INTRODUCTION

Methanol is available from renewable sources, such as biomass, or from non-petroleum sources, such as coal. For this reason it is considered an attractive alternative to gasoline as an automotive fuel. However, it suffers the disadvantage of having a lower enthalpy content than gasoline, which translates into less mileage per gallon of fuel(1). The potential fuel value of methanol can be improved by catalytically decomposing it into syngas prior to its combustion in an internal combustion engine. Syngas, which is also referred to as dissociated methanol, has approximately a 14% higher enthalpy content than methanol. The combustion enthalpies for methanol, syngas ( $2\text{CO} + 4\text{H}_2$ ), and dimethyl ether (a side product of methanol decomposition) is given in Table I. A Chevrolet Citation and a Ford Escort have been retrofitted with catalytic converters in order to demonstrate the feasibility of this process. A schematic of the automotive system is shown in Figure 1. The design and testing of this system was carried out at the Solar Energy Research Institute (SERI). A more

detailed description of the automotive system employed in these studies is available in the literature(2).

At the time this study was initiated, no catalyst had been designed specifically for the decomposition of methanol into syngas in an automotive converter. In order to find an effective catalyst for this process, the following catalyst requirements were defined. First, the catalyst must demonstrate good selectivity for syngas over a large temperature range. Second, the catalyst should be able to withstand high temperatures without deactivating. Third, the catalyst should show significant activity at low temperatures. Fourth, the catalyst should be mechanically strong. Fifth, the catalyst cost should be reasonable. Several catalysts were prepared by placing active metals (Cu, Ni, Pd, and Pt) on a variety of supports (magnesia, silica, alumina) were tested and the results were compared with those obtained from several commercial formulations(3). All of the commercial formulations failed either the first, second or fourth requirements or a combination of those requirements. Palladium and platinum were found to be the best metals for the decomposition of methanol and alumina was found to be the best support, however, the alumina support is also active for the dehydration of methanol into dimethyl ether, which is an undesirable side reaction. Therefore, several catalysts were prepared in our laboratory in which active metals were impregnated onto a variety of modified gamma-alumina supports. The modified supports have a marked effect on the activity, selectivity, and thermal stability of some metals and little effect on others.

The objective of this study is to establish the function of these modified supports in controlling the behavior of the active metal. Many of the initial test and characterization results have been reported in the literature(3,4). However, some of the more interesting catalysts have been studied and characterized in more detail and are discussed below.

## EXPERIMENTAL

The catalysts were tested under the same temperature and flow conditions that would be experienced in the automotive system. The tests were conducted in a microcatalytic plug-flow reactor. Methanol was pumped into a heated inlet and vaporized. The catalyst was mounted on a fritted disk in a quartz tube. The methanol vapor was passed over the catalyst bed and the decomposition products were introduced by a gas sampling valve into a gas chromatograph. The gas chromatograph was equipped with a thermal conductivity detector and a 9 ft. x 1/8 inch stainless steel column packed with Poropak Q. Hydrogen analysis was accomplished by using a 5% hydrogen in helium carrier gas and a subambient program.

The modified supports were prepared by impregnating a gamma-alumina support with a solution containing the nitrate salt of the desired modifying agent. Subsequently, the modified supports were dried at 150°C, calcined at 550°C, and

impregnated with a solution containing either the nitrate or chloride salts of palladium or platinum. The drying and calcining steps were repeated for the finished catalyst. The catalysts were activated in the reactor under a flow of hydrogen at 300°C for 1 hour and at 400°C for 1 hour prior to testing.

Approximately 0.4 grams of 14-20 mesh catalyst particals were tested in each run, using a methanol flow rate of 0.19 g MeOH/g cat.-hr. The methanol was distilled over magnesium turnings and stored over 5A molecular sieve before use. Ultra high purity hydrogen was passed over a Matheson Model 450 purifier.

The total catalyst surface areas were obtained using conventional BET methods. The active metal surface areas were obtained with a volumetric apparatus using hydrogen chemisorption, carbon monoxide chemisorption, and hydrogen-oxygen titration techniques.

For the temperature programmed desorption studies, 0.4 grams of the catalyst were reduced in hydrogen at 400 or 500 °C for 2 hours. The hydrogen was stripped from the catalyst surface in a helium for 15 min. and then cooled in helium to 0°C. Subsequently, several pulses of carbon monoxide were introduced until the surface was saturated. The temperature desorption profile was obtained by increasing the temperature at a rate of 25°C/min. and analyzing the desorption products in a quadrupole mass spectrometer. The temperature programmed desorption apparatus is very similar to that used by other researchers(5). All the gases used during the characterization studies were of Ultra High Purity grade and they were further purified to remove traces of oxygen, water and other impurities.

The catalysts were also characterized before and after testing using a Rigaku x-ray diffractometer, a Perkin Elmer 5000 atomic absorption spectrometer, and a Surface Science SSX-100 x-ray photoelectron spectrometer.

## RESULTS AND DISCUSSION

### Catalyst Testing

All catalysts were tested at 300°C, the average operating temperature of the converter, and at 500 or 550°C to simulate a high temperature excursion. Subsequently, the temperature was lowered to 300°C to check for possible catalyst deactivation. The results of these tests are given in Table II. Each catalyst contains approximately 5 wt.% of the metal oxide modifying agent and a 0.5 wt% Pd or Pt. The modifying agents Li<sub>2</sub>O, MgO, Cs<sub>2</sub>O, and La<sub>2</sub>O<sub>3</sub> are represented in Table II as Li, Mg, and La. The gamma-Al<sub>2</sub>O<sub>3</sub> support is represented as Al. The products observed in these tests were hydrogen, carbon monoxide, methane, carbon dioxide, water, dimethyl ether, and unconverted methanol. The mole % products in Table II are reported on a hydrogen free basis.

To begin with we will only consider the initial activity

of the catalysts at 300°C prior to a high temperature excursion at 550°C. The alumina support (Al) shows almost no activity for the formation of the desired CO decomposition product, but is very active for the formation of dimethyl ether. The formation of dimethyl ether is an exothermic reaction and should be avoided. In the case of the Pd-Al and Pt-Al catalysts, it is obvious that the metal plays the primary role in the production of CO, however, the dehydration activity of the support is still apparent. For those catalysts using the modified supports, Pd-Li-Al, Pd-Mg-Al, Pd-La-Al, Pt-Li-Al, Pt-Mg-Al, and Pt-La-Al the dehydration activity of the catalysts has been eliminated or reduced to an acceptable level. It is interesting to note that the modified supports have a pronounced effect on the initial activity of the Pd metal as indicated by the production of CO, with the Pd-Li-Al showing the lowest activity and the Pd-La-Al showing the highest activity. On the other hand, the initial activity of the Pt metal does not appear to be influenced by the nature of the modifier used.

At 550°C, the modified supports have a pronounced effect on the catalyst selectivity. All the Pt catalysts and the Pd-La-Al catalyst produce substantial amounts of methane, carbon dioxide, and water, while the Pd-Al, Pd-Li-Al, and Pd-Mg-Al catalysts are quite selective for the desired CO product. These results suggest that the latter catalysts have thermally deactivated and the resultant activity and selectivity is really due to the support and not the metal.

The final activity at 300°C, after testing at 550°C, shows all of the Pd catalysts (with exception of the 3% Pd catalyst) have thermally deactivated, while the Pt catalysts show no deactivation or an increase in activity.

The catalyst testing was extended to modified catalysts containing approximately 3 wt% Pd, and the results are shown in Table III. In these tests the hydrogen analysis was included. The effects of the modified supports on the initial and final activities of the catalysts is obvious, with the Pd-La-Al catalyst representing the best case and the Pd-Li-Al catalyst the worst case. The Pd-La-Al catalyst appears to experience a slight loss in activity after a thermal cycle. However, exposing the Pd-La-Al catalyst to repeated thermal cycling over a three day period resulted in no further deactivation. This catalyst was selected for use in the "dissociated methanol car" and has fulfilled all the catalyst requirements with exception of the cost of the material. In any case, it has allowed the feasibility of the process to be demonstrated in an automobile.

#### Catalyst Characterization

The modified supports have a marked influence on the catalyst activity, selectivity and thermal stability. Modified alumina supports may have an important impact on the behavior of metals other than Pd and Pt. The effects of these modified supports may extend to other important chemical reactions which involve hydrogenolysis, dissociation, or hydrogenation steps,

such as, Fischer Tropsch, and methanol synthesis. In order to understand the role of the modified support in controlling the behavior of the active metal component, selected catalysts were characterized using both bulk and surface techniques. Since the Pd-Li-Al and the Pd-La-Al catalysts represent the most extreme cases in activity, selectivity and thermal stability, they were selected for further detailed studies.

The complete thermal deactivation of the Pd-Li-Al catalyst could result from one of the following processes:

- 1) Loss of total surface area due to support sintering.
- 2) Loss of total surface area due to pore blockage.
- 3) Loss of the active Pd metal from the catalyst.
- 4) Sintering of the metal crystallites.
- 5) Migration of the metal into the support.
- 6) Covering the active metal with an inactive material.
- 7) Formation of a new inactive Pd compound.

The first two possibilities were eliminated by measuring the total surface area of the fresh and reduced Pd-Li-Al catalyst using the BET method. There was no significant change in the total surface area and the results are given in Table IV.

The metal content of the fresh, reduced and tested catalysts were determined using atomic adsorption and the results are also given in Table IV. It is apparent that the active metal does indeed remain with the catalyst.

Broadening of the Pd lines in x-ray diffraction would suggest sintering of the metal crystallites was involved. The XRD spectra for both the reduced and tested Pd-Li-Al catalyst is shown in Figure 2. There is no evidence of line broadening, however, all the palladium lines of the tested catalyst have shifted to lower  $2\theta$  values. This suggests that either a new compound has been formed or that the Pd lattice has expanded, possibly due to the palladium forming a solution with another element. These results would also argue against the migration of the Pd metal into the support as a cause for the thermal deactivation.

The catalyst deactivation was also found to be reversible, as shown in Figure 3. Although the catalyst was deactivated at high temperatures, its activity could be restored by recalcining the catalyst in air and reducing in hydrogen. The catalyst demonstrated an activity almost identical to its initial activity. However, the catalyst was again deactivated after a thermal cycle. This result strongly argues against migration of the Pd metal into the support, which should be an irreversible process. It also suggests that the element which is causing the deactivation is easily removed by treatment with oxygen, an example of such an element would be carbon.

XPS analysis of the fresh, reduced, and tested Pd-Li-Al and Pd-La-Al catalysts is shown in Figure 4. These survey scans provided information about the elemental composition of the catalyst surfaces before and after testing. The peaks of most interest are the Pd 3d peaks. For the Pd-La-Al catalyst the Pd is present at the surface of the fresh, reduced, and tested catalyst. In fact, the Pd signal is enhanced after

testing. On the other hand, the Pd-Li-Al catalyst shows that the Pd signal has almost disappeared on the tested catalyst. This would suggest that the catalyst is being covered by some other element. The carbon signal, just to the right of the Pd peak, appears to increase on the Pd-Li-Al catalyst but not for the Pd-La-Al catalyst. A depth profile of the surface was obtained by sputtering the surface with argon ions. The results are shown in Figures 6 and 7. The Pd signal for the Pd-Li-Al catalyst increased as the surface was sputtered away, while the carbon signal disappeared at the same time. The Pd-La-Al catalyst showed little effect with sputtering of the surface.

Finally, temperature programmed desorption/reaction of carbon monoxide from the surface was conducted to study the ability of the two catalysts to disproportionate carbon monoxide into carbon dioxide and carbon. The disproportionation reaction may be the primary source of the carbon for the deactivation of the Pd-Li-Al catalyst, see Figure 5. It is apparent that much more carbon dioxide is produced over the Pd-Li-Al catalyst and the reaction takes place at a much lower temperature. This suggests that the modified supports have a pronounced effect on the surface activity of the Pd metal.

#### SUMMARY

The activity, selectivity, and thermal stability of Pd metal is strongly influenced by the use of the modified supports. This suggests that either the modified support is influencing the behavior of the metal by either controlling the dispersion of the metal crystallites or by exhibiting a strong metal-support interaction.

#### REFERENCES

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- 2) J. Finegold, G.P. Glinsky, and G.E. Voecks, "Dissociated Methanol Citation: Final Report", SERI/TR-235-2083, August 1984.
- 3) S.W. Cowley and S.C. Gebhard, "The Catalytic Decomposition of Methanol into Synthesis Gas for Use as an Automotive Fuel", CSM Quarterly, 7(3), 41 (1983).
- 4) S.C. Gebhard, B.W. Logsdon, and S.W. Cowley, "The Decomposition of Methanol Over Supported Palladium and Platinum Catalysts", manuscript in preparation.
- 5) J.M. Zowtiak and C.H. Bartholomew, J. Catal., 83, 107 (1983).

TABLE I. Combustion Enthalpies for Methanol, Dimethyl Ether, Methane, and Synthesis Gas.

Combustion Reactions	$H_r$ (kcal/mole)	
	400°K	800°K
1. $2\text{CH}_3\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}_2\text{O}$	-322.4	-321.5
2. $\text{CH}_3\text{OCH}_3 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$	-317.1	-316.8
3. $2\text{CH}_4 + 4\text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}_2\text{O}$	-365.0	-341.4
4. $2\text{CO} + 4\text{H}_2 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}_2\text{O}$	-367.7	-371.0

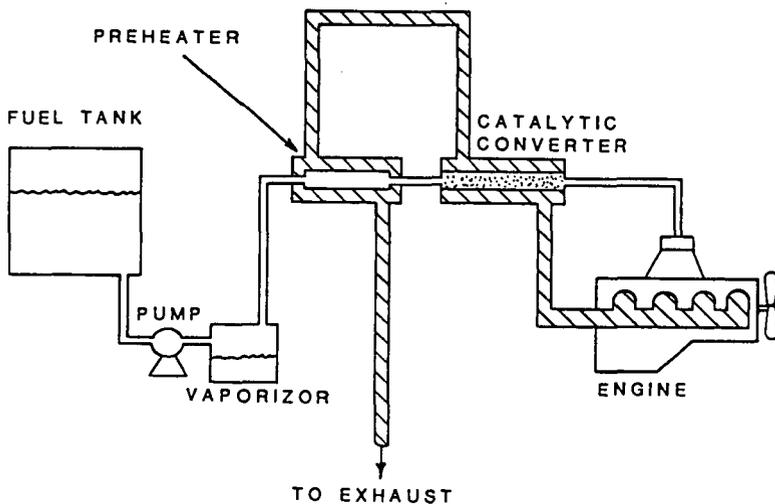


Figure 1. Automotive system for methanol decomposition. The unhatched pathway delineates the transport of fuel toward and into the engine; the hatched pathway illustrates the discharge of exhaust gases from the engine.

TABLE II. Methanol Decomposition Over Pd and Pt Catalysts.

CATALYST*	TEMP. (°C)	%Pd or %Pt	MOLE % PRODUCTS					
			CO	CH <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub> O	CH <sub>3</sub> OH	DME
Al	300	0	0.9	0	0	25.1	47.5	26.6
	550		78.9	7.5	6.7	5.8	0	0
	300		0.9	0	0	25.5	46.7	27.0
Pd-Al	300	0.5	60.8	0.9	0.8	13.5	12.2	21.3
	550		72.5	10.3	6.7	8.1	0.8	0
	300**		0.4	0	0	2.5	95.0	0
Pd-Li-Al	300	0.5	36.5	0	0	1.5	62.0	0
	550		94.3	0	1.3	2.7	1.0	0.8
	300**		1.0	0	0	0.8	98.0	0
Pd-Mg-Al	300	0.5	36.6	0	0	1.5	61.9	0
	550		92.9	1.2	1.3	3.5	0.7	0.5
	300**		0.7	0	0	2.5	95.0	1.8
Pd-La-Al	300	0.5	85.6	0.8	0.7	3.2	9.2	1.5
	500		61.7	2.0	2.6	13.6	7.1	12.9
	300**		-	-	-	-	-	-
Pd-La-Al	300	3.0	85.4	2.4	1.0	5.8	2.7	2.4
	550		18.0	41.8	17.7	22.1	0	0
	300**		83.5	2.0	0.7	7.6	2.5	2.6
Pt-Al	300	0.5	25.2	2.7	1.8	25.4	23.3	21.1
	550		40.9	28.4	13.0	16.4	0.6	0
	300**		35.8	1.5	0.7	22.0	19.3	20.0
Pt-Li-Al	300	0.5	46.8	0.8	0.8	1.0	49.5	0
	550		65.2	16.0	8.1	9.7	0	0
	300**		45.0	0.9	0.6	1.2	51.2	0
Pt-Mg-Al	300	0.5	45.8	0.6	0.5	1.6	51.8	0
	550		52.7	22.0	11.4	12.3	0	0
	300**		50.1	1.0	0.4	2.5	44.5	0
Pt-La-Al	300	0.5	48.3	0	2.0	4.6	42.1	0
	550		26.6	35.5	16.8	19.8	0.6	0
	300**		69.6	0	1.2	2.9	23.0	0

\* Catalyst Wt. = 0.400 g, approx. 5% metal oxide modifier present  
 Space Velocity = 1.9 g MeOH/g cat.-hr.

Pressure = 608.0 mm Hg

\*\* After testing at 500°C

TABLE III. Methanol Decomposition Over Modified 3% Pd Catalysts. Hydrogen Analysis Included in Product Analysis

CATALYST*	TEMP. (°C)	MOLE % PRODUCTS						
		H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub> O	CH <sub>3</sub> OH	DME
Pd-Al	300	57.8	31.0	0.7	0.3	6.5	1.1	2.5
	550	25.6	5.4	31.0	15.8	22.3	0	0
	300**	59.2	32.2	0.8	0.3	5.0	0	0
Pd-Li-Al	300	53.4	29.2	0	0	1.1	16.3	0
	550	60.8	30.2	0.8	2.3	3.0	0.2	2.7
	300**	1.4	0.5	0	0	2.3	96.8	0
Pd-Cs-Al	300	34.8	19.9	0.5	0	4.1	40.6	0
	550	56.7	27.9	6.4	4.2	4.9	0	0
	300**	34.2	18.2	0.3	0	2.5	44.8	0
Pd-La-Al	300	56.7	30.4	0	0	0	13.0	0
	500	33.9	10.5	25.0	14.2	16.1	0	0
	300**	51.6	28.0	0	0	1.7	18.6	0

\* Catalyst Wt. = 0.400 g, approx. 5% metal oxide modifier present  
Space Velocity = 1.9 g MeOH/g cat.-hr.  
Pressure = 612-622 mm Hg

\*\* After testing at 500°C

TABLE IV. Elemental Composition and Surface Analysis of Pd Catalysts.

Catalyst	Catalyst History	Pd Metal* (wt.%)	Metal Oxide** (wt.%)	BET (m <sup>2</sup> /g)	Chemisorp. (mole Pd/g)		
					H <sub>2</sub>	CO	H <sub>2</sub> -O <sub>2</sub>
Pd-Al	fresh	2.6	0	-	-	-	-
	reduced	2.6	-	-	115.1	102.8	107.4
	tested	2.6	-	-	-	-	-
Pd-Li-Al	fresh	2.9	5.0	75.6	-	-	-
	reduced	2.9	-	-	45.7	37.0	-
	tested	2.9	-	75.6	-	-	-
Pd-Cs-Al	fresh	2.8	5.0	-	-	-	-
	reduced	2.8	-	-	67.7	64.5	57.0
	tested	2.9	-	-	-	-	-
Pd-La-Al	fresh	3.4	5.0	-	-	-	-
	reduced	3.3	-	-	66.0	53.8	48.7
	tested	3.4	-	-	-	-	-

\* Wt. % metal was determined by atomic absorption

\*\* Estimated from preparation

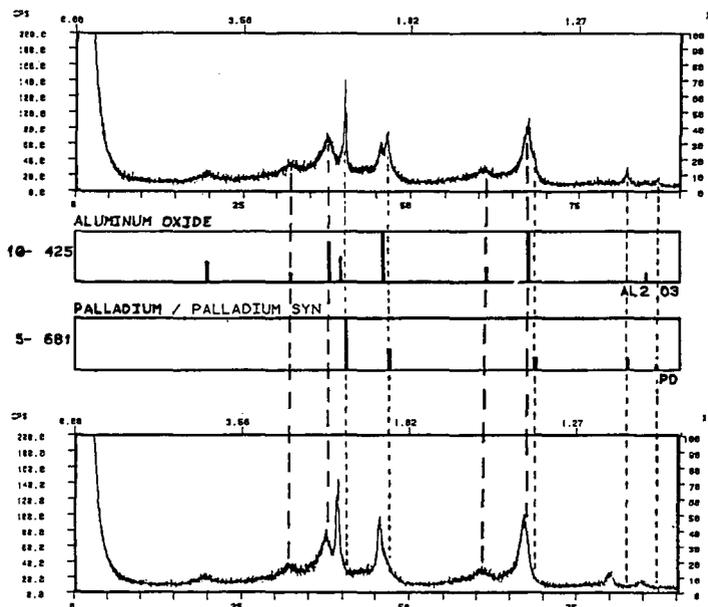


Figure 2. The XRD spectra of a reduced (top) and a tested (bottom) Pd/alumina catalyst modified with lithia.

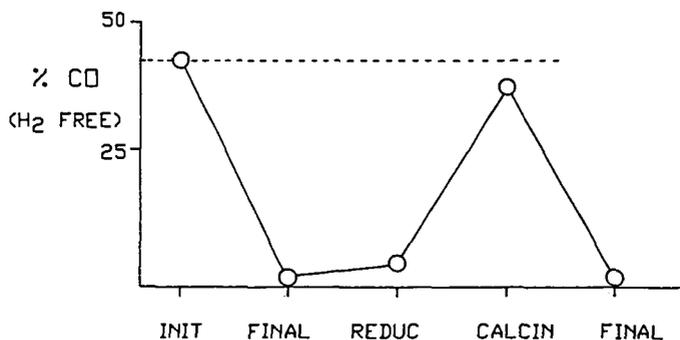


Figure 3. The lithia modified Pd/alumina catalyst always shows severe deactivation (final) after exposure to high temperature, but its activity can be restored after calcining in air and reducing the catalyst (calcin).

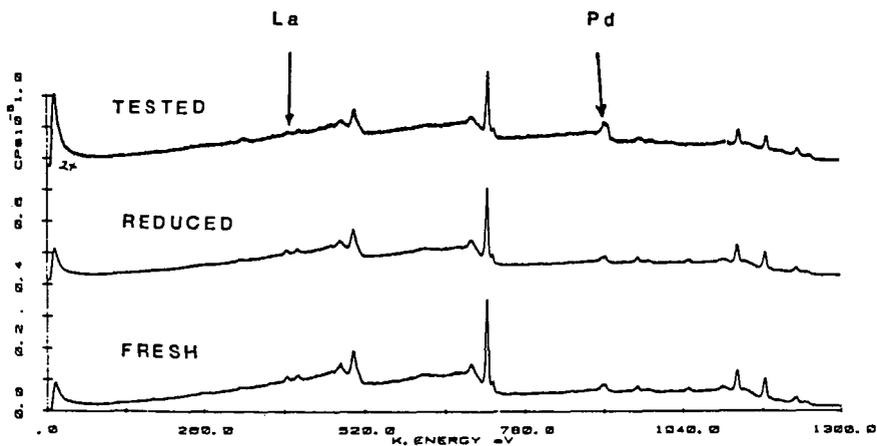
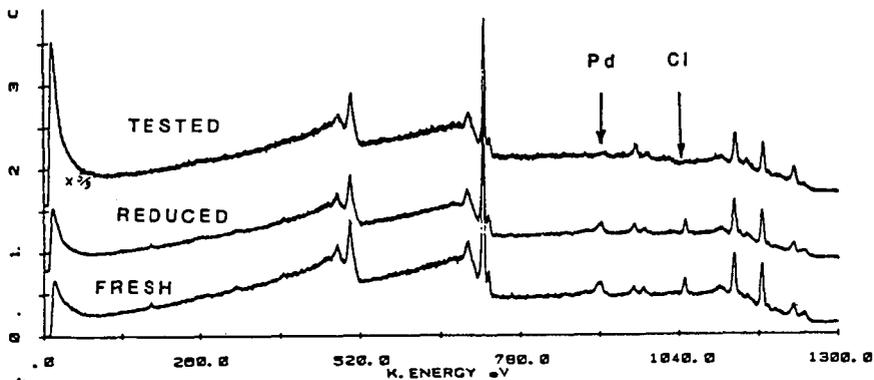


Figure 4. XPS survey scan of a lithia (top) and a lanthana (bottom) modified Pd/alumina catalyst which has been either freshly calcined, reduced, or tested.

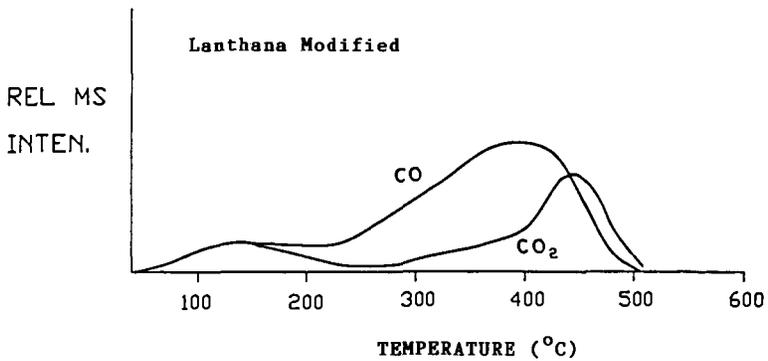
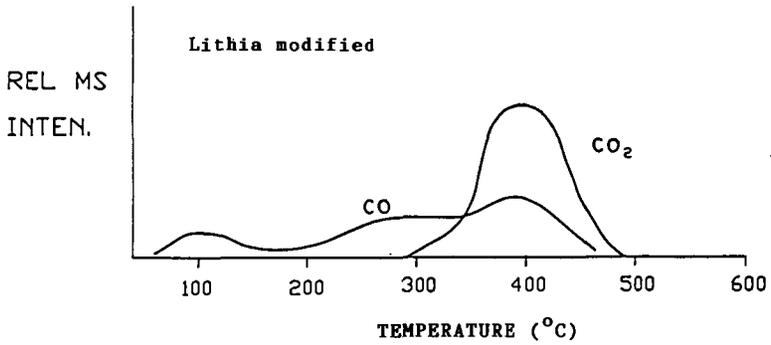


Figure 5. TPD profile of CO from a lithia (top) and a lanthana (bottom) modified Pd/alumina catalyst.

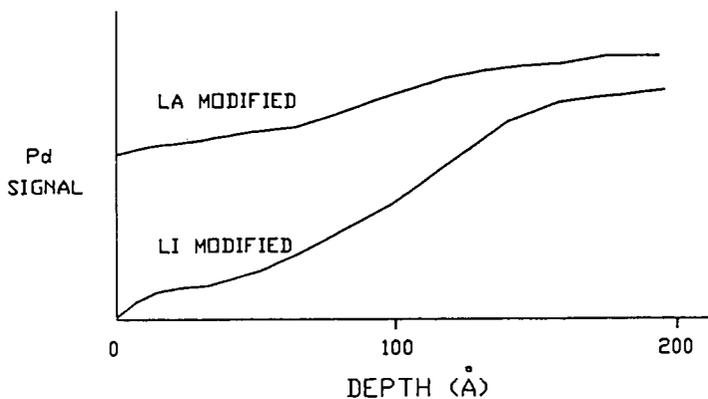


Figure 6. The depth profiles of the XPS Pd<sub>3d</sub> signal for Pd/alumina catalysts modified with lanthana or lithia.

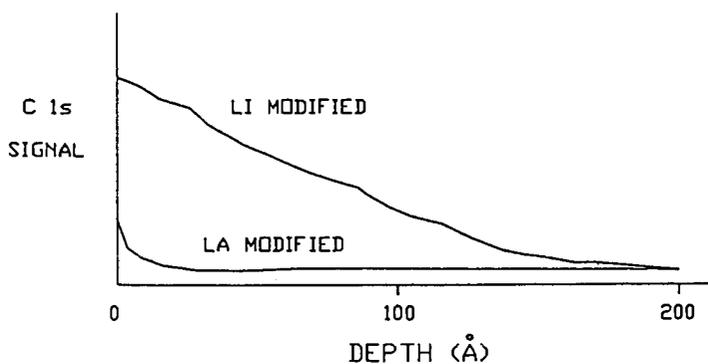


Figure 7. The depth profiles of the XPS C<sub>1s</sub> signal for Pd/alumina catalysts modified with lanthana or lithia.