The Effect of Lanthanum Promoter on the Selectivity of Pd/Zeolite-X in Methanol Synthesis

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The promoting effect of various amounts of lanthanum on Pd/zeolite-X in enhancing selectivity in CO hydrogenation toward methanol/oxygenates has been investigated. The catalysts were characterized by temperature-programmed reduction, O_2–H_2 titration, and temperature-programmed desorption. The dispersion and H_2 chemisorption of Pd/zeolite-X catalysts were almost unchanged on La promotion. The virtually unchanged chemisorption capacity of the Pd/zeolite-X catalysts on La promotion is attributed to the cationic exchange method adopted to introduce La after Pd introduction into the zeolites. The La_2O_3 formed during calcination was partially reduced during reduction with hydrogen due to its contact with palladium. $PdLaO_x$ entities formed thereby trigger the activation of coordinated CO/H_2 and facilitate the hydrogenation of CO to methanol/oxygenates at low temperature. Thus, the Pd sites responsible for methanol synthesis are stabilized by La at low and high pressures. Dimethyl ether, dominant for low La content Pd/zeolite-X catalysts, may be ascribed to the acid sites developed, but other mechanisms cannot be ruled out. The effect of the zeolite matrix lies in the stabilization of $PdLaO_x$ entities, but otherwise it behaves in a similar fashion to other supports. The zeolite lattice, however, ensures the maintenance of small $PdLaO_x$ particles. The turnover frequency values obtained with the optimum La promotion on Pd/zeolite-X are consistent with the reported values observed on Pd/La_2O_3 catalysts. The zeolites are therefore potential alternative supports in the preparation of suitable bimetallic systems. © 1990 Academic Press, Inc.

1. INTRODUCTION

The pioneering work of Poutsma *et al.* (*1*) has prompted many researchers to pursue intensive studies on supported Pd catalysts and to provide an alternative to the presently used Cu-based catalyst for industrial methanol synthesis. Temperature, pressure, type of reactors, and the supports employed to disperse the Pd particles play a vital role in the selectivity shown in the hydrogenation of carbon monoxide. Pd/SiO_2 is known to give methanol selectively at high pressure, while methane and methanol are the main products in flow reactors (*2*) and in circulation reactors (*3*), respectively. On Pd/Al_2O_3 methane was produced under atmospheric pressure (*4*). Pd/zeolite afforded only methane at elevated pressures (*5*), while under atmospheric pressure the proportion of methane dropped to one-fifth

of the products but no methanol was produced (*6*). This anomalous behaviour could be due to the changes in Pd morphology. Recent studies have indicated that addition of Li, La, Mg, or Fe to Pd/SiO_2 catalysts enhanced the activity for methanol but the selectivity shift toward oxygenates is only of marginal importance (*7–12*). In a preliminary communication we reported the promoting effects of La addition to Pd/zeolite-X that led to enhanced methanol selectivity under both atmospheric and higher pressures (*13*).

In the present paper we provide additional experimental results for the understanding of the promoting effects of La on Pd/zeolite-X in the selective synthesis of methanol. The effect of lanthanum on Pd dispersion as well as on H_2 chemisorption is correlated with the selectivity and activity in methanol synthesis. The techniques used

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in this study are temperature-programmed reduction (TPR), O_2–H_2 titration, and temperature-programmed desorption (TPD).

2. EXPERIMENTAL

2.1 Catalyst Preparation

The zeolite Na-X (with a chemical composition of $Na_{86}[Al_{86}Si_{106}O_{384}]$) and $Pd(NH_3)_4Cl_2$ were obtained from Aldrich. Double-distilled water was used for all purposes during the catalyst preparation. The concentrations of Pd (1.9×10^{-4} g-at. Pd per gram sample) and La were determined by X-ray fluorescence (XRF) and occasionally checked by quantitative wet analysis.

PdLa/zeolite-X was prepared by a successive exchange method. First zeolite Na-X was exchanged with palladium to give PdNa/zeolite-X. This was followed by exchange with La to afford PdLa/zeolite-X. The amounts of $Pd(NH_3)_4Cl_2$ and $LaCl_3$ were calculated on the basis of maximum ion exchange capacity to produce the required atomic ratios as given in Table 1. XRF and chemical analysis confirmed that nearly all the metal ions were taken up by the zeolites. The exchange reactions were conducted by adding zeolites to the respective salt solutions (500 ml solution per gram of zeolites) under rapid stirring and subsequent heating at 363 K for 24 h. The samples were washed free of chloride ions and dried at 383 K.

The exchanged zeolite samples were calcined at 573 K (ramping 1 K min⁻¹) in a flow of oxygen (30 cm³ min⁻¹) for 18 h to remove ammonia and were then evacuated at the same temperature for 2 h, passivated, and stored.

2.2 Catalyst Characterization

The promoted and unpromoted catalysts were characterized using temperature-programmed reduction (TPR), O_2–H_2 titration, H_2 chemisorption, and temperature-programmed desorption (TPD) of hydrogen. A flow apparatus was applied in which the PdLaNa/zeolite-X samples were treated in the following way. First, TPR measurements were carried out using 1% H_2 in argon (flow rate 40 cm³ min⁻¹) at 5 K min⁻¹ heating rate in the temperature range between 298 and 723 K. At 723 K the sample was purged with helium for 1 h, after which it was cooled to 373 K. Chemisorption of oxygen at 373 K was followed by hydrogen titration at the same temperature in a stream of argon (20 cm³ min⁻¹). In this hydrogen titration the method of Aben (14) was followed in order to avoid formation of the β-palladium hydride phase. Then the chemisorbed hydrogen was determined by hydrogen TPD using flowing argon (20 cm³ min⁻¹) and a heating rate of 20 K min⁻¹ in the temperature range 373–723 K. Since during oxygen chemisorption the reoxidation of the partially reduced La_2O_3 is unavoidable, the metallic surface area was calculated from the amount of the hydrogen consumed during titration assuming a $1:3$ O_2/H_2 stoichiometry. After reduction the palladium appeared to be X-ray amorphous indicated by the X-ray diffraction pattern.

2.3. Catalytic Reaction

The CO + H_2 reaction was studied in a high-pressure stainless-steel tubular reactor (10 cm³) containing 0.3 cm³ of calcined catalyst placed between two plugs of quartz wool. The temperature was controlled with a precision of 2 K. The activity data are expressed in mol s⁻¹ g_{cat}^{-1} units.

The calcined catalyst was first flushed

TABLE 1

H_2 Uptake for Different Samples Observed during TPR Experiments

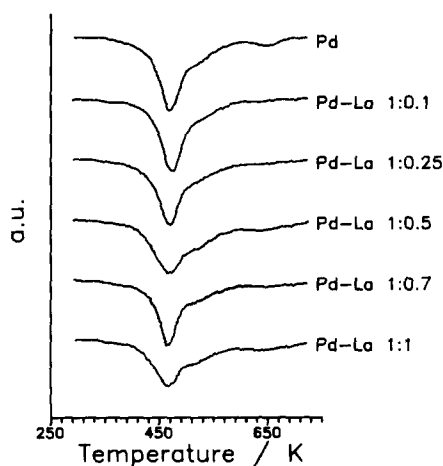| Catalyst	Atomic ratio La/Pd	H_2 consumption during TPR (mol g⁻¹ × 10⁴)	Excess H_2 consumption over Pd/zeolite-X (mol g⁻¹ × 10⁵)
PdNaHX	0	3.33	0
PdLaNaHX	0.1	3.61	2.8
PdLaNaHX	0.25	3.70	3.7
PdLaNaHX	0.5	4.27	9.4
PdLaNaHX	0.7	4.30	9.7
PdLaNaHX	1.0	3.87	5.4

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FIG. 1. TPR curves for various PdLaNaH/zeolite-X samples after calcination at 570 K for 18 h.

with nitrogen and reduced at 723 K in flowing hydrogen for 5 h.

The premixed feed gas ($CO/H_2 = 1/2$) was purified by passing it through activated carbon, prereduced manganese acetate impregnated on molecular sieve and finally through silica gel. A buffer gas cylinder, from which the gas mixture passed into the reactor, was applied to maintain the required pressure. The outflow was controlled by a valve usually set at 25 cm³ min⁻¹ and periodically measured by a wet test meter. The effluent gases were ana-lysed during a Packard-437 gas chromatograph and a Shimadzu integrator. The separation was carried out using a Chromosorb 101 column (100–200 mesh), which was connected to an exit of the reactor via a six-way sampling valve.

3. RESULTS

3.1. TPR Measurements

TPR experiments were conducted to characterize the reducibility of Pd/zeolite-X catalysts without and with La promoter. The spectra for H_2 consumption during TPR are shown in Fig. 1. The TPR spectrum of the PdNaH/zeolite-X consists of a single peak at 483 K and a shoulder at 523 K with a total H_2 uptake of 3.33×10^{-4} mol. The spectrum for the La-promoted catalyst exhibits a peak shift for the shoulder from 523 to 543 K. Moreover, the peak characteristic of the nonpromoted sample at 650 K disappears. Both peaks are progressively broadened as the concentration of La increases. The total H_2 consumption for all promoted samples is larger than the uptake by the unpromoted catalysts, as given in Table 1.

3.2. $H_2–O_2$ Titrations

The dispersion of the catalysts measured by $O_2–H_2$ titration after reduction at 720 K is given in Table 2. The results show that

TABLE 2

O_2 Chemisorption, H_2 Titration, H_2 TPD, and Metal Dispersion of Pd-Containing and Lanthanum-Promoted Zeolites

Catalyst	Atomic ratio La/Pd	Chemisorbed O_2 at 373 K (mol g⁻¹ × 10⁵)	H_2 titration at 373 K (mol g⁻¹ × 10⁵)	Disp. (%)	H_2 desorbed (mol g⁻¹ × 10⁵)	Disp. (%)
PdNaHX	0	2.40	6.46	23	2.43	26
PdLaNaHX	0.1	2.45	6.69	24	2.14	23
PdLaNaHX	0.25	2.34	7.31	26	2.32	25
PdLaNaHX	0.5	3.32	7.81	28	2.64	28
PdLaNaHX	0.7	2.97	7.30	27	2.55	27
PdLaNaHX	1	2.60	7.43	26	2.23	24

Note. Metal loading is 2 wt% Pd for all the catalysts. The partial exchange of sodium by hydrogen is expected especially for La salts which tend to hydrolyse with coordinated water (Ref. (31)).
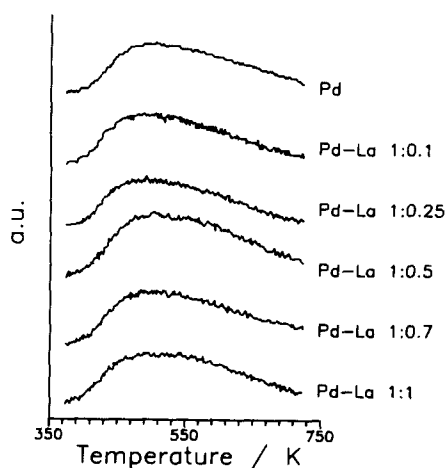
FIG. 2. Hydrogen TPD curves for various PdLaNaH/zolite-X samples

the dispersions of the unpromoted and the La-promoted Pd/zeolite-X are very similar and only a slight increase in the dispersion for the promoted sample can be observed.

3.3. H_2 TPD

The TPD spectra for H_2 desorption from the PdNaH/zeolite-X and the La-promoted catalysts reduced at 720 K are shown in Fig. 2. The initial coverage of the chemisorbed hydrogen atoms is based upon the amount of hydrogen desorbed up to 723 K. The chemisorption capacity of the lanthanum-promoted Pd/zeolite-X is slightly higher than that of unpromoted Pd zeolite,

as is evident from Table 2. Figure 2 shows a featureless broad peak for the La-promoted catalyst. However, the peak position is centered at somewhat higher temperature than that observed for the unpromoted sample. In addition to this, the spectra of the La-promoted Pd/zeolite-X show a broader peak.

3.4. CO Hydrogenation to Form Oxygenates

The catalytic activities and selectivities of the lanthanum-promoted and unpromoted Pd/zeolite-X in the CO hydrogenation were determined under 1 bar and medium pressures in the range of 470–570 K, maintaining the conversion level in the effluents at steady state below 5%. Under 1 bar pressure it is generally observed that the formation of methane is increased with rising temperature for all promoted catalysts, methanol being the exclusive oxygenate (dimethylether, DME, formation is negligible). On the other hand, under 10 bar pressure, in addition to methanol, which is the main product, DME, ethanol, propanol and diethyl ether are also produced.

The steady state of catalysts with high activity and selectivity for methanol formation was attained after ca. 6 h time-on-stream. Prior to this, in the transient period, hydrocarbons were the main products.

Tables 3 and 4 as well as Figs. 3 and 4

TABLE 3

Kinetic Parameters of Pd Catalysts for CO Hydrogenation

Catalyst	Atomic ratio La/Pd	Rate of CH_3OH formation (mol s^{-1} g^{-1} $\times$ 10^5)	TOF CH_3OH (s^{-1} $\times$ 10^3)	Selectivity to methanol (%)
PdNaHX	0	0.15	0.34	48
PdLaNaHX	0.1	1.00	2.3	86
PdLaNaHX	0.25	1.17	2.5	90
PdLaNaHX	0.5	1.40	2.7	93
PdLaNaHX	0.7	2.92	5.8	93
PdLaNaHX	1.0	1.32	2.8	88

Note. Pressure: 1 bar; temperature: 508 K.

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TABLE 4

Kinetic Parameters of Pd Catalysts for CO Hydrogenation

Catalyst	Atomic ratio La/Pd	Rate of oxygenates formation (mol s^{-1} g^{-1} × 10^5)	TOF (s^{-1} × 10^3)	Selectivity to oxygenates (%)
PdNaHX	0	0	0	0
PdLaNaHX	0.1	2.12	5.0	76
PdLaNaHX	0.25	5.44	11.7	85
PdLaNaHX	0.5	6.00	11.4	90
PdLaNaHX	0.7	6.57	12.9	92
PdLaNaHX	1.0	5.40	12.1	76

Note. Pressure: 10 bar; temperature: 508 K.

illustrate the effect of the lanthanum promoter on palladium/zeolite-X catalysts for the activities and selectivities of methanol formation. By the addition of La to Pd/zeolite-X in an atomic ratio of La/Pd = 0.7, there is a distinct shift in oxygenate selectivity from 48 to 93% and from a very low value to 92% under 1 bar and 10 bar pressures, respectively.

The activity for the methanol formation has risen 7 to 20-fold with lanthanum promoters when compared to unpromoted catalyst under 1 bar pressure. Under 10 bar pressure the rate of methanol formation is

in the range 2.1–6.6 × 10^{-7} mol g^{-1} s^{-1}. The ratio of La/Pd = 0.7 appeared to be the optimum for selectivity and activity in methanol/oxygenate formation under both 1 and 10 bar pressures, as evidenced in Figs. 3 and 4.

Under 10 bar pressure the DME formation is diminished with the increase of lanthanum concentration, as indicated in Fig. 5. At higher content of lanthanum no dimethylether is produced.

Figure 6 illustrates the effect of space velocity on PdLaNaH/zeolite-X catalyst for methanol formation. At high space velocity
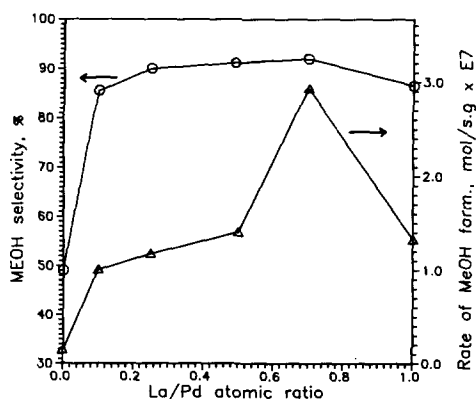

FIG. 3. Rate and selectivity of CH$_3$OH formation vs Pd/La ratio in PdLaNaH/zeolite-X samples. T = 508 K, pressure = 1 bar.
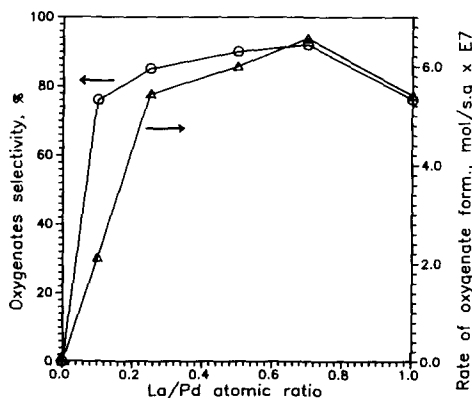

FIG. 4. Rate and selectivity of oxygenate formation vs Pd/La ratio in PdLaNaH/zeolite-X catalysts. T = 508 K, pressure = 10 bar.
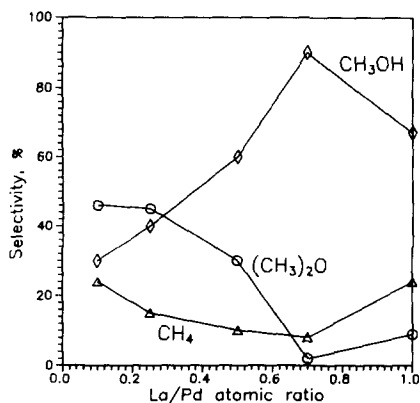
FIG. 5. CH_3OH, $(CH_3)_2O$ and CH_4 selectivities vs Pd/La ratio in PdLaNaH/zeolite-X catalysts. $T = 508$ K, under 10 bar pressure.
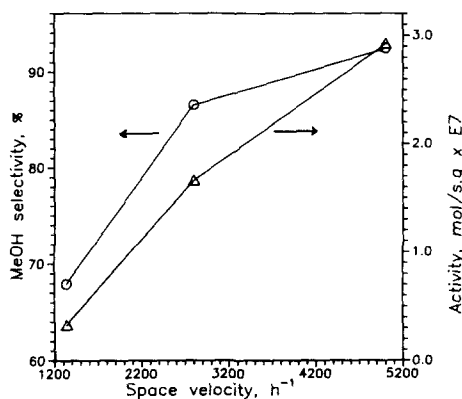

FIG. 6. Effect of space velocity on the selectivity and activity of methanol measured on PdLaNaH/zeolite-X sample with Pd/La = 0.7 ratio; $T = 508$ K, under 1 bar pressure.

(5000 h^{-1}) the activity and selectivity toward methanol are increased. At low space velocity (1400 h^{-1}) the activity drops by sixfold and the oxygenate selectivity is lowered to 68%.

A shift in selectivity toward higher alcohols with increasing pressure is presented in Table 5. Significant amounts of ethanol and propanol have been formed using PdLaNaH/zeolite-X (La/Pd = 1) catalyst under 40 bar pressures.

The Arrhenius plot of the reaction rate for CH_3OH formation on LaPdNaH/zeolite-X (La/Pd = 0.7) sample under 1 bar pressure vs reciprocal temperature results

in an apparent energy of activation of 75 kJ mol^{-1}.

4. DISCUSSION

The promotion effect on Pd-based catalysts normally active in the CO hydrogenation to form oxygenates has been widely discussed in the literature. It is now generally accepted that rare earth elements serve as excellent promoters for palladium supported on silica and alumina (10, 15). The rare earth oxides can be partially reduced and the interface formed between the reduced oxides and the metallic palladium makes the metal partially electron deficient,

TABLE 5

Formation of Higher Alcohols at 553 K over PdLaNaHX Zeolites with Pd/La Ratio of 1

Pressure (bar)	Oxygenates selectivities (%)				Total oxygenates (%)	Paraffin selectivities (%)		Total hydrocarbon (%)
	CH_3OH	DME	C_2H_5OH	C_3H_7OH		CH_4	C_{2+}	
1	44	—	—	—	44	56	—	56
10	78	—	—	—	78	9	13	22
20	76	2	5	—	83	7	10	17
40	58	2	17	2	79	8	13	21

which can be identified by the proportionality between methanol formation and the Pd^{n+} ions extracted (16). The acid–base properties of the support can also be influenced by addition of promoters such as MgO, K, Na, Cl, but a direct relationship has not yet been found (17). Nevertheless, MgO has been proved to be a good promoter, e.g., for Pd/SiO_2 catalysts, for which a tenfold activity increase in methanol formation was observed (18). However, the effect of magnesia has not been fully clarified because even the dispersion of palladium particles was not significantly enhanced.

As far as the promoting mechanism of lanthanum is concerned, the situation is further complicated by the electron donation toward palladium, which was studied by XPS (19). An excess negative charge was observed on Pd by the binding energy measured in the Pd $3d$ region and this is opposite to that observed earlier (17).

Two questions should be addressed when zeolite is used as support. First, one must ask whether the size of the metal particles is confined by the supercage or whether the metal migrates to the external surface of the zeolite matrix. Second, one needs to know how the nature of particles is affected by the zeolite framework itself. Following the identical treatment applied here, Tzou et al. (20) demonstrated for Pt/faujasite-X that the platinum dispersions are located exclusively within the zeolite framework and the platinum particles, which are mostly 1 nm in size, are fully accessible for chemisorption and reaction. Some fragmentations of the zeolite framework are suggested but these are accommodated in defect zeolite lattice sites. However, the zeolite structure is maintained intact.

Mössbauer evidence was also given that the iron in tetrahedral coordination in the supercage of Na/zeolite-X played a decisive role in developing a good Fischer–Tropsch catalyst mainly because of the stabilization effect of the small particle size (21). Furthermore, it was also established

that iron and palladium formed bimetallic particles inside the zeolite supercage, the size of the particles being confined by the size of the supercage (22). The presence of bimetallic particles has also been confirmed for other systems, e.g., for the Pt–Mo bimetallic catalysts supported on Na/zeolite-Y (23, 24).

These advantages, i.e., the size of the zeolite supercage and the formation of bimetallic particles, make the application of zeolites feasible. In PdNaH/zeolite-X the amount of the H_2 uptake during TPR provides evidence for the reduction of palladium and partly of La_2O_3. The excess hydrogen uptake with increasing promoter concentration is indicative of the partial reduction of lanthanum oxide in contact with palladium. Similar observations have been made by Rieck and Bell for Pd/SiO_2 promoted by La_2O_3 and TiO_2 (10, 14, 15). The peak broadening is likely to be due to the less homogeneous distribution of the Pd oxide particles as a result of the increasing interface with La_2O_3. However, this does not necessarily mean an increase in metallic Pd dispersion as indicated by the particle size values observed by H_2 chemisorption and O_2–H_2 titration. Similar observations have been made for other lanthana-promoted and titania-promoted Pd/SiO_2 (10, 25, 26).

The hydrogen TPD spectra demonstrate that the chemisorption of hydrogen is not suppressed. The virtually unchanged chemisorption capacity on the La promoter, which is in contrast to the results obtained by Rieck and Bell, is attributed to the preparation method. These results confirm that the ion exchange method, even in sequential manner, is easily adaptable for Pd and La in zeolites and that after decomposition in oxygen, palladium and lanthanum are maintained in the supercage in the vicinity of each other. Hence the lack of the drastic change in hydrogen chemisorption, at least in the concentration range studied, which indicates that the palladium sites are not decorated by the lanthanum

promoter, as observed by Rieck and Bell (*10*).

The catalytic activity of the promoted Pd zeolite increases by several-fold and the selectivity toward oxygenates is shifted from 50 to 90% under 1 bar pressure, whereas at higher pressure no methanol is formed on PdNaH/zeolite-X. On the other hand, in the latter case the activity of the promoted catalyst is much higher than that observed under 1 bar pressure. The striking selectivity shift toward oxygenates caused by lanthanum promotion over that of other La-promoted Pd/SiO$_2$ samples obtained by Driessen *et al.* (*16*) and Rieck and Bell (*10*) is highly impressive.

The value of the activation energy, 75 kJ mol^{-1}, observed for the PdLaNaH/zeolite-X with optimum performance (La/Pd = 0.7) is in full agreement with the activation energies reported for Pd catalysts on other supports, such as SiO$_2$, ranging from 57 to 84 kJ mol^{-1} (*15, 27–29*), MgO, ZnO, Al$_2$O$_3$, TiO$_2$, ZrO$_2$, and SiO$_2$–Al$_2$O$_3$, ranging from 57 to 92 kJ mol^{-1} (*27, 29*), and La$_2$O$_3$, ranging from 73 to 88 kJ mol^{-1} (*15, 30*). Thus, these results suggest that the zeolite does not essentially affect the properties of LaO$_x$ interfacing the Pd particles. Since the activation energy of PdLaNaH/zeolite-X (La/Pd = 0.7) is in full agreement with that obtained for Pd/La$_2$O$_3$, we can speculate that a similar mechanism is operative in the La-promoted Pd zeolite catalysts. The TOF values under 10 bar and 508 K for the lanthanum-promoted catalyst are in the range of 5–12.1 × 10^{-3} s^{-1} based on the chemisorption of fresh catalyst. This is comparable to the values of 13.4 × 10^{-3} s^{-1} measured under 14.6 bar and 523 K for Pd/La$_2$O$_3$ and based upon the chemisorption on used catalyst (*15*).

As the space velocity increases, the activity and selectivity toward methanol are increased. At low space velocities a sudden fall of selectivity is observed, in contrast to the results obtained by Lunsford on Pd/SiO$_2$ (*5*).

As the pressure is raised, the shift in oxy-genates leads to the formation of significant amount of higher alcohols. No ethanol formation for Pd/La$_2$O$_3$ (*15, 30*) and Pd/SiO$_2$ (*1, 30*) at high pressures has been observed. This result suggests that the secondary reactions, responsible for the formation of higher alcohols, are facilitated in zeolite cages. Ethanol formation by RhFe clusters in zeolite cages even under 1 bar pressure gives credence to this speculation (*31*).

For the interpretation of the lanthanum promotion effect in zeolite the following arguments should be taken into consideration:

—La$_2$O$_3$ is partially reduced during activation of the catalysts;

—no change in the dispersion occurs indicating that after reduction the palladium particles interfaced to lanthanum oxide remain in the supercage;

—methanol is not formed at high pressure in the absence of lanthanum but in its presence CH$_3$OH and higher oxygenates are produced regardless of the pressure.

Although palladium with excess negative charge exists on pure La$_2$O$_3$ support (*19*), its existence has not been proven when lanthanum is present as promoter, only when La/Pd atomic ratio well exceeds 1. In the case of Pd/ZSM-5 catalysts promoted by lanthanum and studied by XPS, 0.7-eV shift was measured toward lower BE, but here the Pd/La atomic ratio was over 1.5. (*32*). In our case the activity and selectivity were found to be optimum at an atomic ratio of Pd/La = 0.7, above which a drastic change was observed. This probably means that at the optimum Pd/La ratio no excess negative charge has been built up on palladium.

Conversely, if extra electron charge exists, it would make a contribution to the backdonation to the antibonding orbitals in the adsorbed CO, by which C–O dissociation would be promoted and methane selectivity would increase, which is not the case. On the other hand, so far methanol selectivity was always connected to the presence of electron-deficient palladium regardless of

whether it was ionic (*16*) or whether it was formed by alloying (*22*).

In the zeolite supercages an interaction between palladium and the highly ionic environment via partially reduced PdO_x can be envisaged. This results in methanol formation under 1 bar pressure but at higher reactant pressure this palladium oxide interface is diminished due to its reduction to larger metallic particles to a great extent. Methanol activity, therefore, vanishes. On the other hand, in the presence of LaO_x the interface containing Pd^{n+} is increased and stabilized, but the electron flow may be directed toward the zeolite matrix rather than to the palladium particles. Thus, the electron deficiency on the palladium being in the interface is maintained and even increased upon raising the lanthanum concentration.

The weakening of the carbon–metal bond in the chemisorbed CO molecule on La-promoted palladium is further supported by TPD studies of chemisorbed methanol in the presence of preadsorbed CO (*10, 33*). Not only is the amount of methanol adsorbed enhanced by lanthanum, but more preadsorbed CO molecules can be displaced in a suface reaction. This results in the enhanced methanol activity and selectivity.

The hydrogen required for hydrogenation of the nondissociatively chemisorbed CO molecule to form formyl species is supplied from the metallic part of the palladium particles. The decrease of methanol activity and selectivity at the highest lanthanum concentration can be ascribed to a diminishing of the palladium oxide surface as a result of being covered with LaO_x entities.

Under 40 bar pressure higher alcohols are also formed. As the H_2 + CO mixture provides a highly reducing atmosphere, the metallic part of palladium is extended and another mechanism becomes operative. Namely, CO molecules are dissociated on Pd particles to produce higher hydrocarbons, and CO insertion follows. This mechanism does not require electron-deficient palladium particles (*17*).

The mechanism of the dimethylether (DME) formation does not seem to be fully elucidated. DME formation is negligible or inconsistent under 1 bar pressure, while under 10 bars the DME/CH_3OH ratio decreases as the La concentration is raised. After La addition in small amounts the formation of dimethylether is predominant.

There are two possible explanations. First, Brønsted sites are known to be responsible for the DME formation on decomposition of methanol (*27*). The La^{3+} ions substituted into the Pd/zeolite-X lattice in low concentration tend to split the coordinated water molecule heterolytically to form $[La(OH)_2]^+$ and protons. On this strong Brønsted acid site DME formation takes place easily. On the other hand, at high concentration of lanthanum the Brønsted acid sites are close to one another and consequently dissociation takes place to a lesser extent and weak Brønsted acid sites are formed (*34*). Hence, at high concentrations of lanthanum the DME formation is diminished.

For the second explanation a primary reaction between methyl and methoxide radicals can be suggested instead of dehydration of methanol in a secondary process. Methyl radicals always exists on metallic palladium and methoxide species can be stabilized on the support (*35*). As the lanthanum concentration is enhanced the relative contribution of methyl radicals decreases and thus the DME formation diminishes.

5. CONCLUSIONS

The virtually unchanged chemisorption capacity of the Pd zeolite catalyst on La promotion is attributed to the cationic exchange method adopted to introduce La after Pd exchange into the zeolite. The excess of hydrogen taken up during TPR for the La-promoted Pd catalyst when compared with that of the Pd zeolite suggests that the La_2O_3 formed during calcination and existing in contact with Pd has been reduced.

The high activity and selectivity for methanol or oxygenate formation are prob-

ably to be attributed to the small Pd particles interfaced to LaO$_x$ and stabilized by the zeolite supercages. The activation energy obtained for the lanthanum-promoted palladium zeolite with the optimum performance is in the range of that observed on other supports, especially on Pd/La$_2$O$_3$. It is suggested that the zeolite supercages provide only stabilization to the Pd-containing LaO$_x$ particles and thereby may prevent coalescence of the metallic particles.

The dominant DME formation for low lanthanum content Pd/zeolite-X is due to either development of strong Brønsted acid sites by hydrolysis of lanthanum salts with coordinated water or a surface interaction between methyl and methoxide radicals.

It is inferred with the CO molecule is activated on the Pd–LaO$_x$ interface, which is enhanced by increasing lanthanum content, and is hydrogenated to a formyl group by the hydrogen atoms activated on the metallic Pd sites. For higher alcohol formation probably a CO insertion mechanism is responsible.

REFERENCES

1. Poutsma, M. L., Elek, L. F., Ibarbia, P. A., Risch, A. P., and Rabo, J. A., *J. Catal.* **52**, 158 (1978).
2. Vannice, M. A., *J. Catal.* **50**, 228 (1977).
3. Kikuzono, T., Kagami, S., Onishi, T., and Tamaru, K., *Faraday Disc.* **72**, 135 (1982).
4. Vannice, M. A., and Garten, R. L., *Ind. Eng. Chem. Prod. Res. Dev.* **18**, 186 (1979).
5. Fajula, F., Anthony, R. G., and Lunsford, J. H., *J. Catal.* **73**, 237 (1982).
6. Mahya, A., Simard, F., Lemay, G., Adnot, A., Kaliaguine, S., and Monnier, J., *Appl. Catal.* **33**, 55 (1987).
7. Deligianni, H., Mieville, R. L., and Peri, J. B., *J. Catal.* **95**, 465 (1985).
8. Fukushima, T., Araki, K., and Ichikawa, J., *J. Chem. Soc. Chem. Commun.,* 148 (1986).
9. Fukuoka, A., Kimura, T., and Ichikawa, M., *J. Chem. Soc. Chem. Comm.,* 428 (1988).
10. Rieck, J. S., and Bell, A. T., *J. Catal.* **99**, 278 (1986).
11. Kelly, K. P., Tatsumi, T., Uematsu, T. Driscoll, D. J., and Lunsford, J. H., *J. Catal.* **101**, 396 (1986).
12. Rieck, J. S., and Bell, A. T., *J. Catal.* **100**, 305 (1986).
13. Choudary, B. M., Lázár, K., Matusek, K., and Guczi, L., *J. Chem. Soc. Chem. Commun.,* 592 (1988).
14. Aben, P. C., *J. Catal.* **10**, 224 (1968).
15. Sudhakar, C., and Vannice, M. A., *J. Catal.* **95**, 227 (1985).
16. Driessen, J. M., Poels, E. K., Hindermann, J. P., and Ponec, V., *J. Catal.* **82**, 26 (1983).
17. van der Lee, G., and Ponec, V., *Catal. Rev. Sci. Eng.* **29**, 183 (1987).
18. Lietz, G., Nimz, M., Völter, J., Lázár, K., and Guczi, L., *Appl. Catal.* **45**, 71 (1988).
19. Fleisch, T., Hicks, R. F., and Bell, A.T., *J. Catal.* **87**, 398 (1984).
20. Tzou, M. S., Teo, B. K. and Sachtler, W. M. H., *J. Catal.* **113**, 220 (1988).
21. Lázár, K., Choudary, B. M., and Guczi, L., *Solid State Ionics,* **32/33**, 1000 (1989).
22. Lázár, K., Nimz, M., Lietz, G., Völter, J., Guczi, L., *Hyperfine Interact.* **41**, 657 (1988).
23. Tri, T. M., Candy, J.-P., Gallezot, P., Massardier, J., Primet, M., Védrine, J. C., and Imelik, B., *J. Catal.* **79**, 396 (1983).
24. Tri, T. M., Massardier, J., Gallezot, P, and Imelik, B., *J. Catal.* **85**, 244 (1984).
25. Rieck, J. S., and Bell, A. T., *J. Catal.* **96**, 88 (1985).
26. Rieck, J. S., and Bell, A. T., *J. Catal.* **99**, 262 (1986).
27. Ryndin, Yu. A., Hicks, R. R., Bell, A. T., and Yermakov, Yu, *J. Catal.* **70**, 287 (1981).
28. Berube, M. N., Sung, B., and Vannice, M. A., *Appl. Catal.* **31**, 133 (1987).
29. Rieck, J. S., and Bell, A. T., *J. Catal.* **103**, 46 (1987).
30. Hicks, R. F., and Bell, A. T., *J. Catal.* **91**, 104 (1985).
31. Rao, L. F., Fukuoka, A., and Ichikawa, M., *J. Chem. Soc. Chem. Commun.,* 458 (1988).
32. Fleisch, T. H., Hicks, R. F., Bell, A. T., Regalbuto, J. R., Thomson, R. T., Lane, G. S., and Wolf, E. E., to be published.
33. Guo, X., Xu, Y., Zhai, R., Zhu, K., and Huang, J., *Pure Appl. Chem.* **60**, 1307 (1988).
34. Ward, J. W., in "Zeolites, Chemistry and Catalysis" (J. A. Rabó, Ed.), p. 118. Amer. Chem. Soc., Washington D.C., 1976.
35. Guczi, L., Hoffer, T., Shestov, A. A., and Tétényi, P., *Chem. Eng. Comm.* **83**, 75 (1989).