

CHAPTER V

RESULTS AND DISCUSSION

The supported palladium catalysts prepared and evaluated in this study were 2%Pd/SiO₂, 2%Pd/0.5%La₂O₃/SiO₂, and 2%Pd/3%La₂O₃/SiO₂. All fresh catalysts were characterized by Atomic Absorption Spectroscopy (AAS), x-ray powder diffraction (XRD), BET surface area, and CO adsorption. Afterwards, they were evaluated their activities and selectivities within a microflow reactor at 200, 300, 400 and 500°C for 5 hr, respectively. After the reaction, used catalysts were characterized by TPO method in order to determine amount of coke and location of coke depositing over catalysts. The catalytic activity and selectivity for ethanol decomposition are presented in Figures 5.6 through 5.8, and product distribution are shown in Figures 5.10 through 5.21. TPO patterns are illustrated in Figures 5.22 through 5.25.

5.1 Catalyst characterization

5.1.1 Catalyst characterization of metal content and BET surface area

The metal (Pd) content of modified Pd catalysts was obtained directly from AAS. Since AAS provided the amount of lanthanum in analysis, lanthanum amount was simplified by stoichiometry to lanthanum oxide content and presented in Table 5.1. Additional data of BET surface area for all studied catalysts was also included in Table 5.1.

Table 5.1 The composition and BET surface area of Pd catalysts

Catalysts	% Pd content	% La ₂ O ₃ content	BET surface area (m ² /g)
2%Pd/SiO ₂	1.9	0	270
2%Pd/0.5%La ₂ O ₃ /SiO ₂	1.9	0.4	265
2%Pd/3%La ₂ O ₃ /SiO ₂	1.9	2.9	254

It shows that the analysis of palladium and lanthanum oxide (lanthana) content in the catalysts are close to the values as expected in the preparation method. Besides, an increase in lanthana loading gradually decreases in surface area. It is possible that the decrease of BET surface area was referred to the agglomeration of the silica particles due to the modification was induced by the presence of lanthana. The reaction agglomeration between La_2O_3 and SiO_2 was confirmed in the further section (XRD discussion).

5.1.2 Catalyst characterization by x-ray diffraction

XRD was used to identify the crystalline phases present in the freshly calcined and tested catalysts. In addition, the average crystallite diameter of supported crystallites was determined using a line broadening method. The catalysts with a higher metal dispersion (or smaller crystallite diameter) were expected to have higher activity for ethanol decomposition, due to an increase the metal active sites.

The XRD line patterns of a SiO_2 support, $0.5\%\text{La}_2\text{O}_3/\text{SiO}_2$, and $3\%\text{La}_2\text{O}_3/\text{SiO}_2$ are shown in the Figure 5.1. SiO_2 , $0.5\%\text{La}_2\text{O}_3/\text{SiO}_2$, and $3\%\text{La}_2\text{O}_3/\text{SiO}_2$ show a single broad peak at approximately 22 degrees 2θ , which is the characteristic of the short-range order presented in amorphous silica. The line pattern for pure crystalline La_2O_3 has peaks at 16, 26.2, 27, 39.5 and 49 degrees 2θ (Figure 5.2). There was no evidence of crystalline La_2O_3 presented on $0.5\%\text{La}_2\text{O}_3/\text{SiO}_2$, and $3\%\text{La}_2\text{O}_3/\text{SiO}_2$. The disappearance of a crystalline pattern for La_2O_3 indicated that either it was highly dispersed over the SiO_2 surface or it was formed with Si to amorphous La-Si phase.

As shown in Figure 5.1, silica peak was observed to be broaden and lowered in peak height with lanthana loading increase. It would be anticipated that lanthana could probably react with silica and form $\text{La}_2\text{Si}_2\text{O}_7$. The result agreed with a discussion by Vidala and coworkers [21]. However, the $\text{La}_2\text{Si}_2\text{O}_7$ spectra could not be detected in XRD spectra in low loading, and it will show up in higher lanthana loading than 10%.

Palladium oxide was not experimented with XRD. The diffraction pattern for palladium oxide was thus obtained from the American Society for Testing Material (ASTM) Power Diffraction File. The major lines are at 33.8, 42.0, 54.8, 60.7 and 71.4 degrees 2θ [22]. The XRD patterns of the fresh catalysts (SiO_2 , 0.5% $\text{La}_2\text{O}_3/\text{SiO}_2$, and 3% $\text{La}_2\text{O}_3/\text{SiO}_2$) are shown in Figure 5.3. The XRD patterns of catalysts got more broaden in a major line characteristic, when lanthana was increased. This presented catalyst contained highly dispersed palladium oxide. A highly dispersed palladium oxide was expected because a polar oxide would be expected to wet the polar surface of silica or lanthana rather than aggregating into an approximate spherical shape. As the results, the XRD pattern of palladium oxide on silica looked similar to those of palladium oxide lanthana-modified silica. The average crystallite diameter was calculated from the line broadening. The average crystallite diameters of palladium on lanthana-modified silica and on silica supports are shown in Table 5.2.

Table 5.2 Calculated average crystallite diameter (see Appendix C)

Catalysts	Crystallite diameter (Å)
2%Pd/ SiO_2	55
2%Pd/0.5% $\text{La}_2\text{O}_3/\text{SiO}_2$	40
2%Pd/3% $\text{La}_2\text{O}_3/\text{SiO}_2$	34

Thus, modification of silica with lanthana improved the dispersion of palladium.

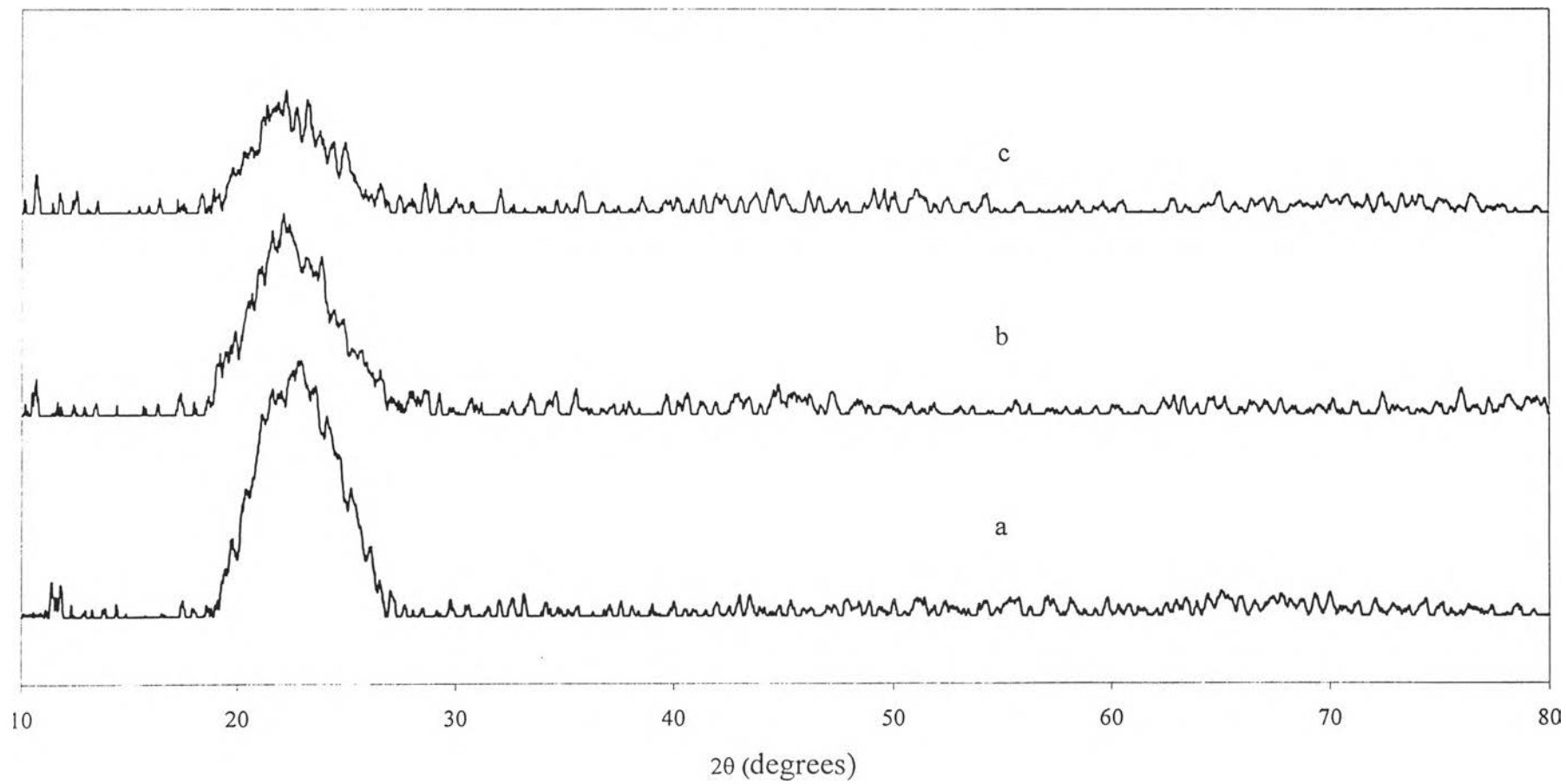


Figure 5.1 XRD spectra of (a) SiO_2 , (b) 0.5% $\text{La}_2\text{O}_3/\text{SiO}_2$ and (c) 3% $\text{La}_2\text{O}_3/\text{SiO}_2$.

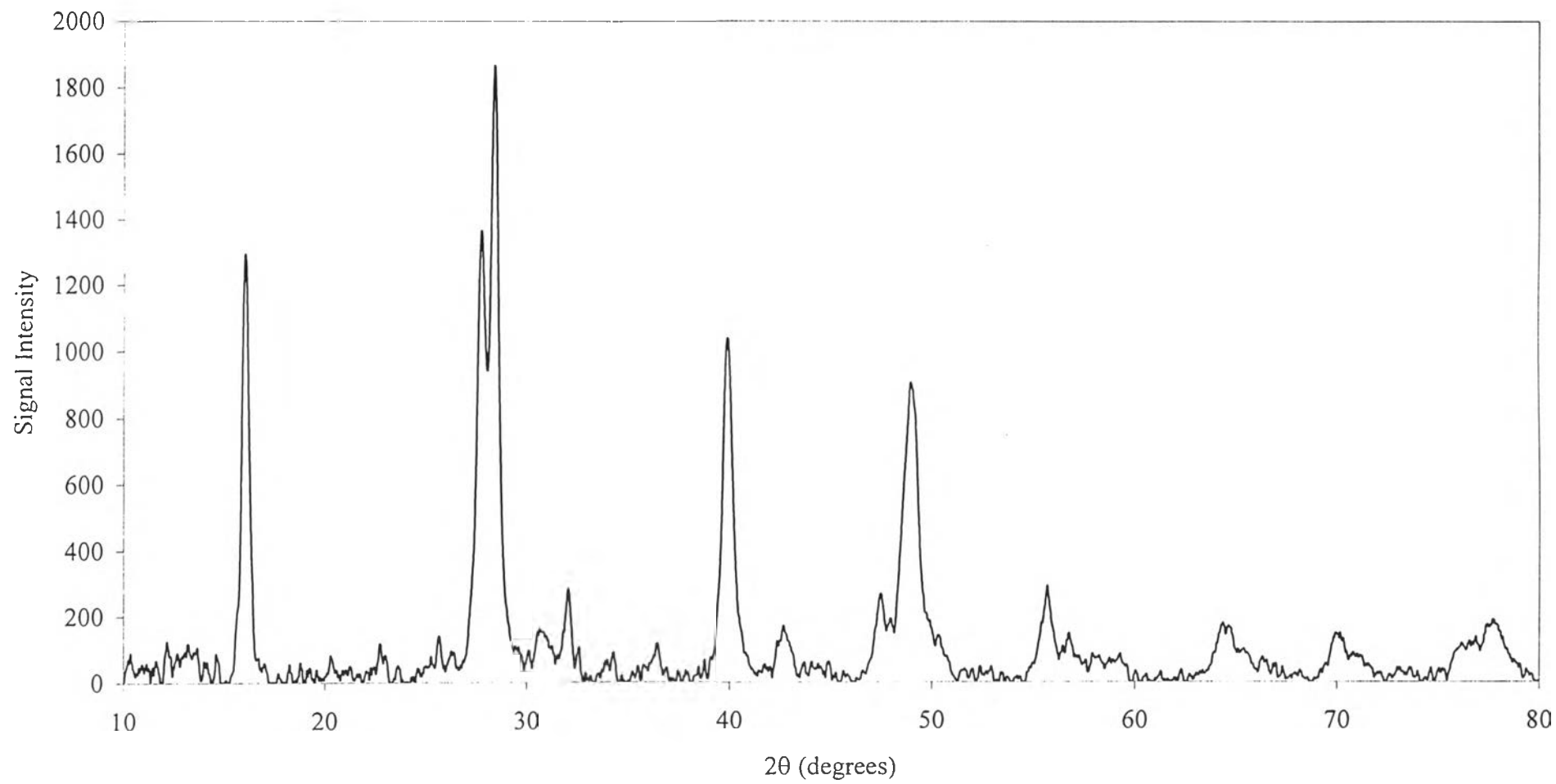


Figure 5.2 XRD spectra of pure lathana.

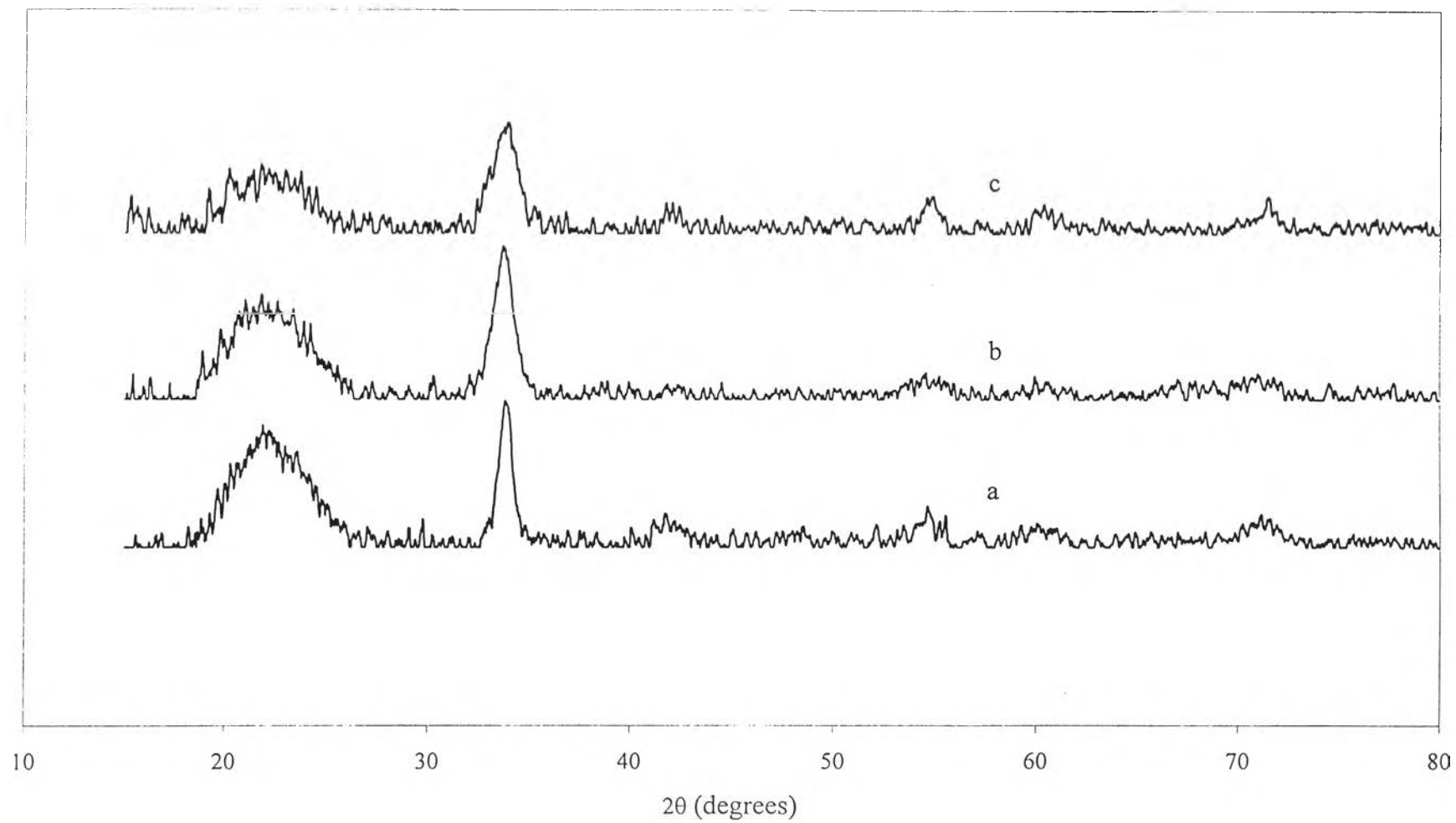


Figure 5.3 XRD spectra of (a) 2%Pd/SiO₂, (b) 2%Pd/0.5%La₂O₃/SiO₂ and (c) 2%Pd/3%La₂O₃/SiO₂.

5.1.3 CO adsorption

In order to confirm that lanthana-modified assisted the dispersion of palladium over catalyst surface, the CO adsorption was investigated. The CO adsorption presents the numbers of available active sites. The results are shown in Table 5.3. As expected, increased active sites were found with increasing lanthana loading. The result was correspondent with smaller crystallite diameter presented in Table 5.2.

Table 5.3 Number of active sites of fresh catalysts (see Appendix D)

Catalysts	Number of active sites (sites/g cat)
2%Pd/SiO ₂	3.11×10 ¹⁸
2%Pd/0.5%La ₂ O ₃ /SiO ₂	3.66×10 ¹⁸
2%Pd/3%La ₂ O ₃ /SiO ₂	4.23×10 ¹⁸

The characteristic of catalysts was changed by the addition of lanthana as described above. However, it is better to investigate whether this kinds of change affect positively or negatively to ethanol decomposition. In the next section, the results and discussion upon the effect by lanthana will be presented. Spent catalysts for all operating conditions were measured the remaining active sites, as listed in Table 5.4. The data will be used in the discussion in section 5.2 and 5.3.

Table 5.4 Number of active sites of spent catalysts after 5 hr TOS

Catalysts	Reaction temperature(°C)			
	200	300	400	500
2%Pd/SiO ₂	2.14×10 ¹⁸	7.11×10 ¹⁷	6.93×10 ¹⁷	4.43×10 ¹⁷
2%Pd/0.5%La ₂ O ₃ /SiO ₂	2.63×10 ¹⁸	2.60×10 ¹⁸	6.12×10 ¹⁷	3.61×10 ¹⁷
2%Pd/3%La ₂ O ₃ /SiO ₂	2.93×10 ¹⁸	3.01×10 ¹⁸	2.97×10 ¹⁷	2.21×10 ¹⁷

5.1.4 Differential thermal analysis (DTA)

Differential thermal measurements have been used for studies of the thermal behavior of material. An important use of differential thermal analysis is for the generation of phase diagrams and the study of phase transition.

The differential thermograms of SiO_2 , 2%Pd/ SiO_2 , 2%Pd/0.5% La_2O_3 / SiO_2 , and 2%Pd/3% La_2O_3 / SiO_2 are shown in Figure 5.4. From this figure, the thermograms of all catalysts are similar to a thermogram of pure silica. The same pattern of palladium catalysts and pure silica indicated that their catalytic phases were not changed during an increase in temperature. As these results, it was shown that phase of all catalysts was stable under the operation temperature range. All peaks in this figure are addressed to be endothermic. It would be speculated that water still retains in catalysts.

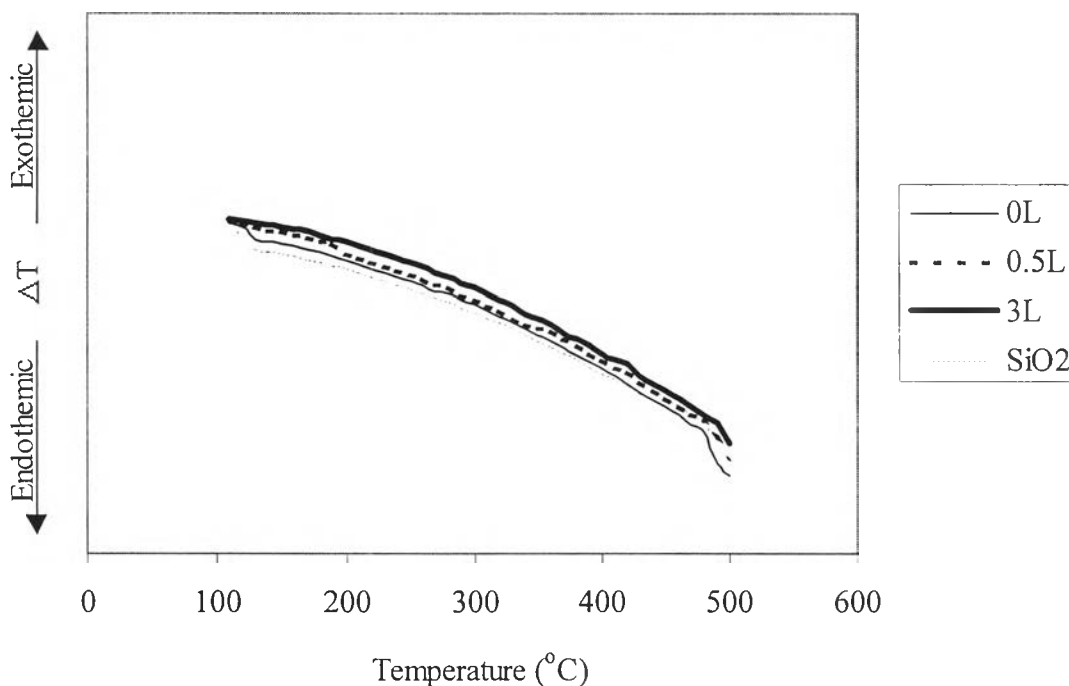


Figure 5.4 Differential thermograms of SiO_2 , (0L) 2%Pd/ SiO_2 , (0.5L)%Pd/0.5 La_2O_3 / SiO_2 , and (3L) 2%Pd/3% La_2O_3 / SiO_2 .

5.2 Activity and selectivity of ethanol decomposition

The reaction effluent from the reactor was identified and evaluated by an on-line gas chromatograph. Expected chemicals such as carbon monoxide, methane, hydrogen, carbon dioxide and acetaldehyde were calibrated in order to further provide the reaction activity and selectivity.

The conversion (activity) and selectivity for ethanol decomposition reaction are defined as follows:

$$\% \text{ conversion} = \frac{(\text{Mole ethanol input} - \text{Mole ethanol output}) \times 100}{\text{Mole ethanol input}}$$

$$\% \text{ Selectivity} = \frac{(\text{Mole of carbon in carbon monoxide and methane}) \times 100}{\text{Mole of carbon in ethanol input} \times \% \text{ conversion}}$$

5.2.1 Blank test of supports

A blank test was investigated under ethanol decomposition. Silica with the same amount of catalyst was placed inside the reactor, while other factors were kept unchanged. It was carried out in temperature program with the range of 200-500°C. In each step, the reaction was carried out continuously for 3 hr in order to ensure the results. The results as activity based on ethanol decomposition are reported in Figure 5.5. It was obviously found that there was an insignificant of conversion taken place at the temperature condition at 200 and 300°C, which was found approximately 2-3%. The activity appeared higher at the temperature of 400 and 500°C. For example; conversion of ethanol to ethylene at 400°C for 2%Pd/SiO₂, 2%Pd/0.5%La₂O₃/SiO₂, and 2%Pd/3%La₂O₃/SiO₂ are 12, 9, and 3%, respectively. Similar to those results, conversions were found 23, 19, and 12%, respectively, at 500°C. The effluent was detected and identified as ethylene and trace of acetaldehyde. As the results, it was proposed that lanthana inhibited ethanol dehydration to ethylene. These activities of support SiO₂ were useful for further discussions.

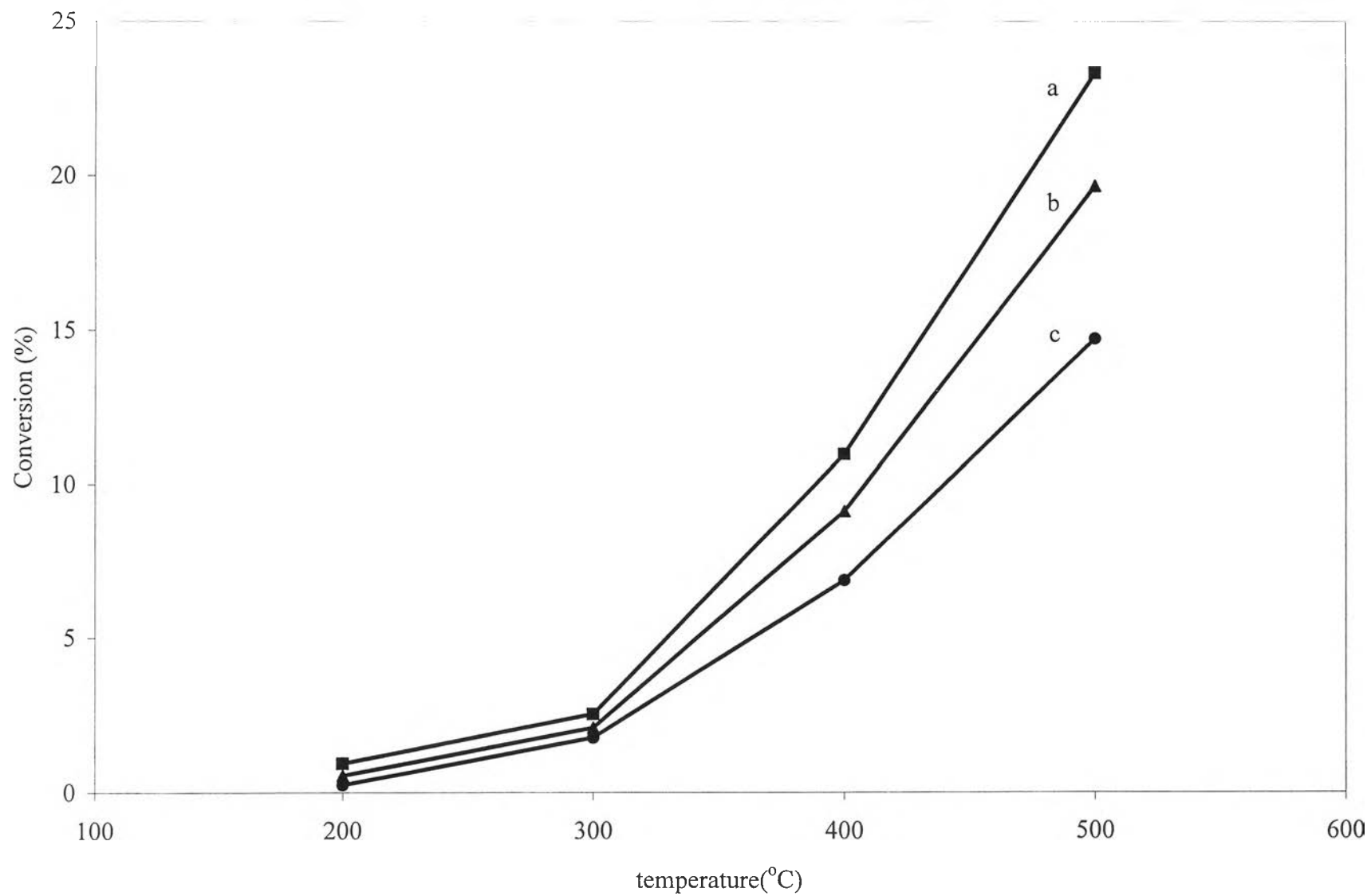


Figure 5.5 Conversion of ethanol over (a) SiO₂, (b) 0.5%La₂O₃/SiO₂, and (c) 3%La₂O₃/SiO₂ as a function of temperature.

5.2.2 Ethanol decomposition at 200°C

The effluent, which was indicated at this condition, was carbon monoxide, methane, hydrogen, carbon dioxide and acetaldehyde. The distributions of effluent upon each catalyst were shown in Figures 5.10-5.12. The primary products were hydrogen, carbon monoxide, and methane. Ethylene, diethyl ether and ethane were not found at this condition. According to the involved reactions described previously, only ethanol dehydrogenation and acetaldehyde decomposition (as seen in equations 3.2 and 3.3) took place while ethanol dehydration produced ethylene could not be attributed. This confirmed that ethanol dehydration to ethylene was not thermodynamically favorable at this condition, as already presented in chapter 3. Carbon dioxide, by-product, was found, referred to the water-gas shift reaction, in small amount (less than 1%). Therefore, this water-gas shift reaction was excluded from this consideration. Upon the feasibility of all expected involved reaction, it was found that at this temperature, ethanol decomposition would dominate. At this temperature all the catalysts showed low conversion. The average ethanol conversions were 10, 12, and 16% over 2%Pd/SiO₂, 2%Pd/0.5%La₂O₃/SiO₂, and 2%Pd/3%La₂O₃/SiO₂, respectively (see Figure 5.6). The average selectivities were 73, 78, and 81% over 2%Pd/SiO₂, 2%Pd/0.5%La₂O₃/SiO₂, and 2%Pd/3%La₂O₃/SiO₂, respectively (see Figure 5.4).

According to high negative value of ΔG_r (see Figure 3.2), it would contribute high conversion (more than 70%). Therefore, it could be concluded that this condition was still in kinetic region. It is important to note that the lanthana-modified silica supported produced more active and selective catalyst than unmodified silica supported did. This may due to the increase of the dispersion of palladium metal (small crystallite diameter) over lanthana-modified silica supported. The results were correspondent to higher dispersion due to lanthana loading, which was discussed in the previous section (5.1.2). The activities and selectivities for all catalysts were stable throughout 5 hr time on stream. They, thus, showed good thermal stability.

5.2.3 Ethanol decomposition at 300°C

With the operating temperature of 300°C, the catalysts resulted in a marked increase in catalyst activity. The catalysts demonstrated average conversions of 32, 50, and 58 and average selectivities of 42, 59, and 63 for the 2%Pd/SiO₂, 2%Pd/0.5%La₂O₃/SiO₂, and 2%Pd/3%La₂O₃/SiO₂, respectively (see Figure 5.7). It is noted that the selectivity presented here is the average value. The results showed conversion and selectivity of lanthana-modified silica supported catalyst (2%Pd/0.5%La₂O₃/SiO₂, and 2%Pd/3%La₂O₃/SiO₂) were somewhat stable. On the other hand, considering the performance by 2%Pd/SiO₂ catalyst, the activity rapidly decreased from 39 to 26% and selectivity was somewhat decreased from 47 to 37% within 5 hours. Product effluent at this temperature was similar to that at 200°C with some trace amount of acetaldehyde. Moreover, no undesired product like ethylene from a dehydration process was observed which indicated that dehydration reaction is not important at this temperature, as well. The product distribution is shown in Figures 5.13-5.15. Product of acetaldehyde via 2%Pd/SiO₂ was found to be with high amount (9% by mole) therefore, the selectivity to main products (carbon monoxide and methane) was lowered as well, compared to those observed over other catalysts. The distributions were similar, in the term of acetaldehyde, which decreased as increase in lanthana loading, to those at previous 200°C temperature condition. This might due to the higher dispersion of catalysts after the modification. These results suggest that the higher active sites, the higher acetaldehyde decomposition reaction is. This would improve the results of activity and selectivity, consecutively.

The effect of lanthana at this temperature gave the activity and selectivity results similar to those at 200°C. The catalyst employing lanthana-modified supported is significantly more active than unmodified counterpart. These results indicated that both ethanol dehydrogenation and acetaldehyde decomposition increased with the presence of lanthana or in the other words, with higher active sites. However, all catalysts showed a gradual declination in its activity and selectivity especially, 2%Pd/SiO₂. This indicated that some catalyst deactivation might occur. The discussion on this matter will be in detail in section 5.3.

5.2.4 Ethanol decomposition at 400°C

The activity and selectivity of catalysts performed at 400°C are plotted in Figure 5.8. The catalysts demonstrated average conversions of 49, 43, and 16 and average selectivities of 52, 53, and 28 for the 2%Pd/SiO₂, 2%Pd/0.5%La₂O₃/SiO₂, and 2%Pd/3%La₂O₃/SiO₂, respectively. As seen, the results obtained at this temperature condition were different from those at lower temperature conditions (200 and 300°C). Lanthana-modified supported showed lower activity at 400°C than those observed at 300°C, while 2%Pd/SiO₂ still gave conversion at 400°C higher than that at 300°C.

Considering the product distribution, with 2%Pd/SiO₂ catalyst, acetaldehyde was appeared, while it was found much more in both modified palladium catalysts, as shown in Figures 5.16-5.18. As known, Pd metal active site promoted the ethanol dehydration to ethylene, which was believed to be a main coke precursor for this system. Due to lanthana promotes good dispersion of Pd metal over catalyst supports, this may increase the sites to generate both reactions and coke. The more coke generated, the more deactivation of catalysts was. This can be happened only by the condition that metal active site contains its size diameter bigger than the critical size of coke [23]. Therefore, when the catalyst activity was declined by both itself and number of active sites, the ethanol decomposition could not perform completely.

Ethanol decomposition requires two steps. For incomplete reaction, only the first step was appeared, while the second step was hard to deal with. As shown, the first step is the step for ethanol dissociation to produce acetaldehyde and hydrogen. This might be a reason that a lot of acetaldehyde was found at high content over lanthana loading, as presented in Figure 5.18. It was found that acetaldehyde generated by 8.0, 9.6, and 48.8% by mole due to the increase of lanthana loading. By the accumulation of coke to all catalysts, the activity then declined gradually, especially for 2%Pd/3%La₂O₃/SiO₂. The selectivity (carbon atom to methane and carbon monoxide) was also found to be lower since carbon atom in ethanol converted not completely to acetaldehyde.

It is interesting to concern the remaining active sites after the operations. Therefore, all spent catalysts were measured through the number of active sites. Lanthana-modified catalysts lose their active sites more than lanthana unmodified catalyst, as presented in Table 5.4. This corresponds to the amount of coke found. According to the results, lanthana was unable to assist selectively to syngas. This expected that the size of metal sites might be bigger than its critical size.

The water-gas shift reaction also occurred over this condition. The consideration should not be emphasized since carbon dioxide was found with trace amount.

5.2.5 Ethanol decomposition at 500°C

The activity and selectivity of catalysts performed at 500°C are plotted in Figure 5.9. The catalysts demonstrated average conversions of 97, 95, and 93 and average selectivities of 58, 55, and 50 for the 2%Pd/SiO₂, 2%Pd/0.5%La₂O₃/SiO₂, and 2%Pd/3%La₂O₃/SiO₂, respectively. It was obviously that at this temperature condition, all catalysts showed activities over those at any studied temperatures. Refer to the blank test, it was known that ethanol dehydration to ethylene occurred at this condition even over a support. Therefore, there was no doubt for having high activity and low selectivity. It was hardly distinguishable catalyst performance to the effect of lanthana loading, since all of them provided very high activity. Some acetaldehyde might possibly decompose to carbon monoxide and methane at higher temperature according to an extremely endothermic reaction. This was caused to have higher selectivity than the results obtained at 400°C.

With a high possibility of ethylene production, coke should be formed and it caused the catalyst activity and selectivity. It was found that, the selectivities of catalysts at this temperature decreased with higher rate than at 400°C. For example, with 2%Pd/0.5%La₂O₃/SiO₂, selectivity (400°C) decreased from 50 to 42%, while selectivity at 500°C decreased from 63 to 49%.

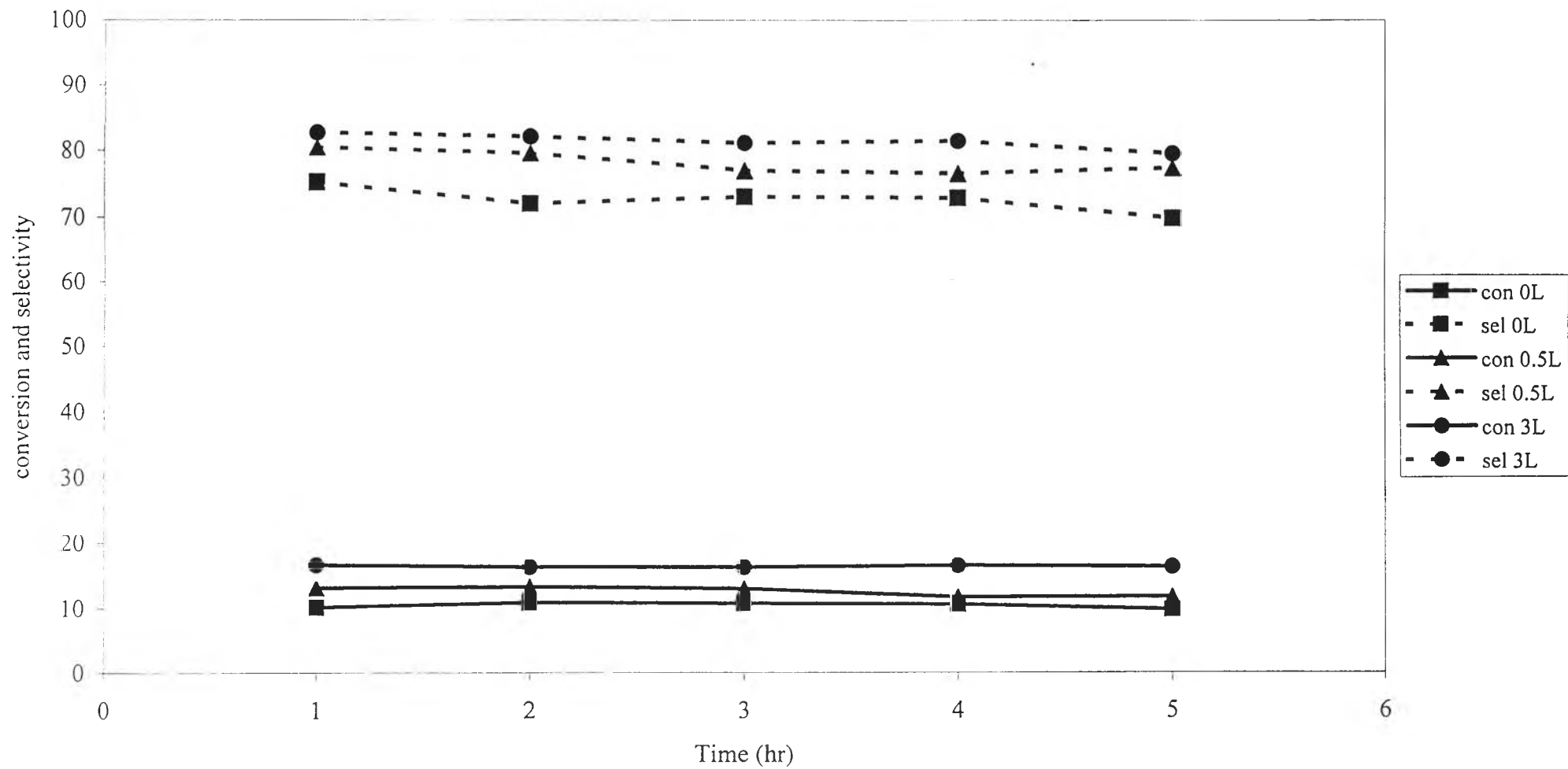


Figure 5.6 Conversion and selectivity with time at 200°C (0L) 2%Pd/SiO₂, (0.5L) 2%Pd/0.5%La₂O₃/SiO₂ and (3L) 2%Pd/3%La₂O₃/SiO₂.

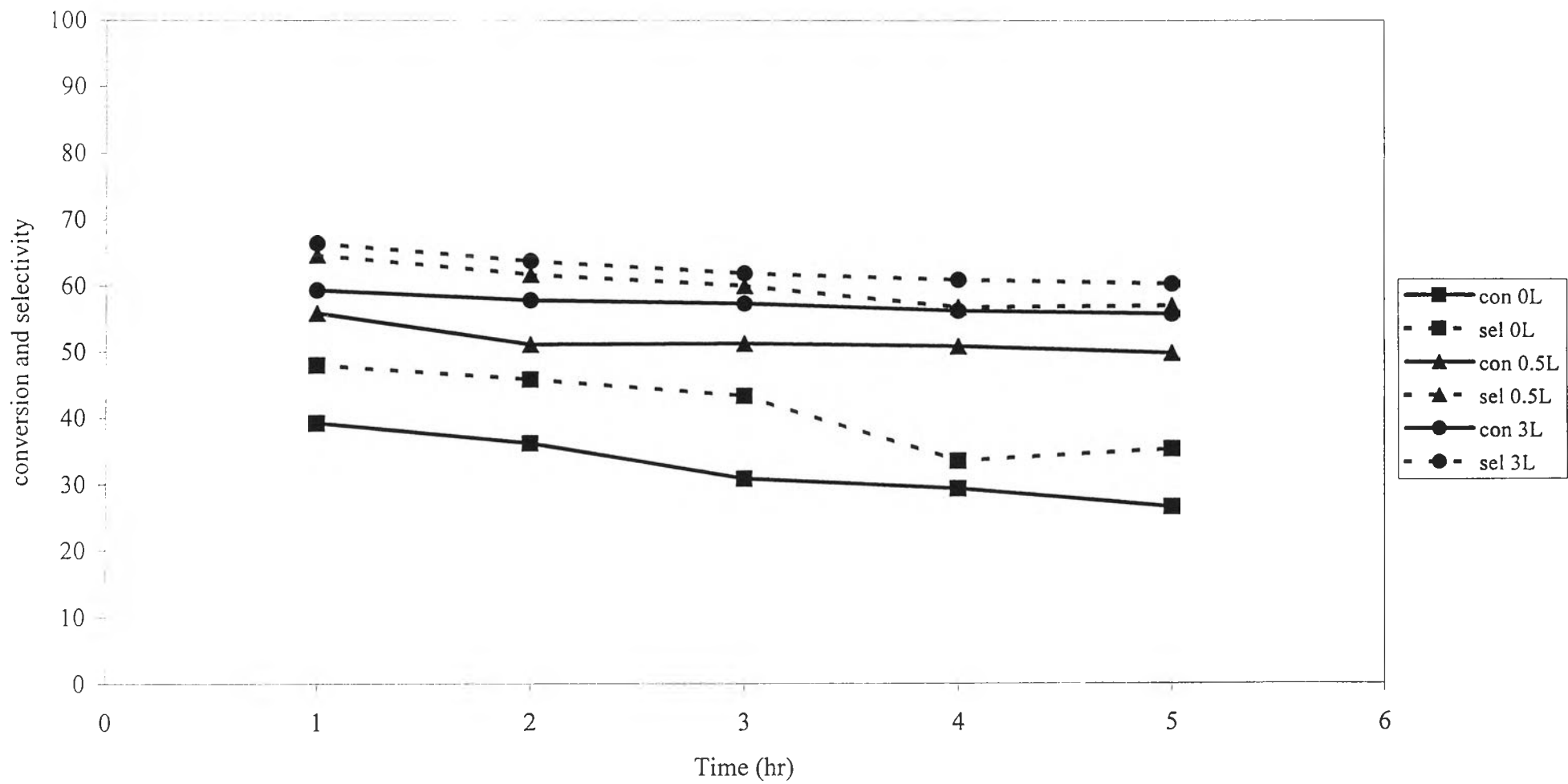


Figure 5.7 Conversion and selectivity with time at 300°C (0L) 2%Pd/SiO₂, (0.5L) 2%Pd/0.5%La₂O₃/SiO₂ and (3L) 2%Pd/3%La₂O₃/SiO₂.

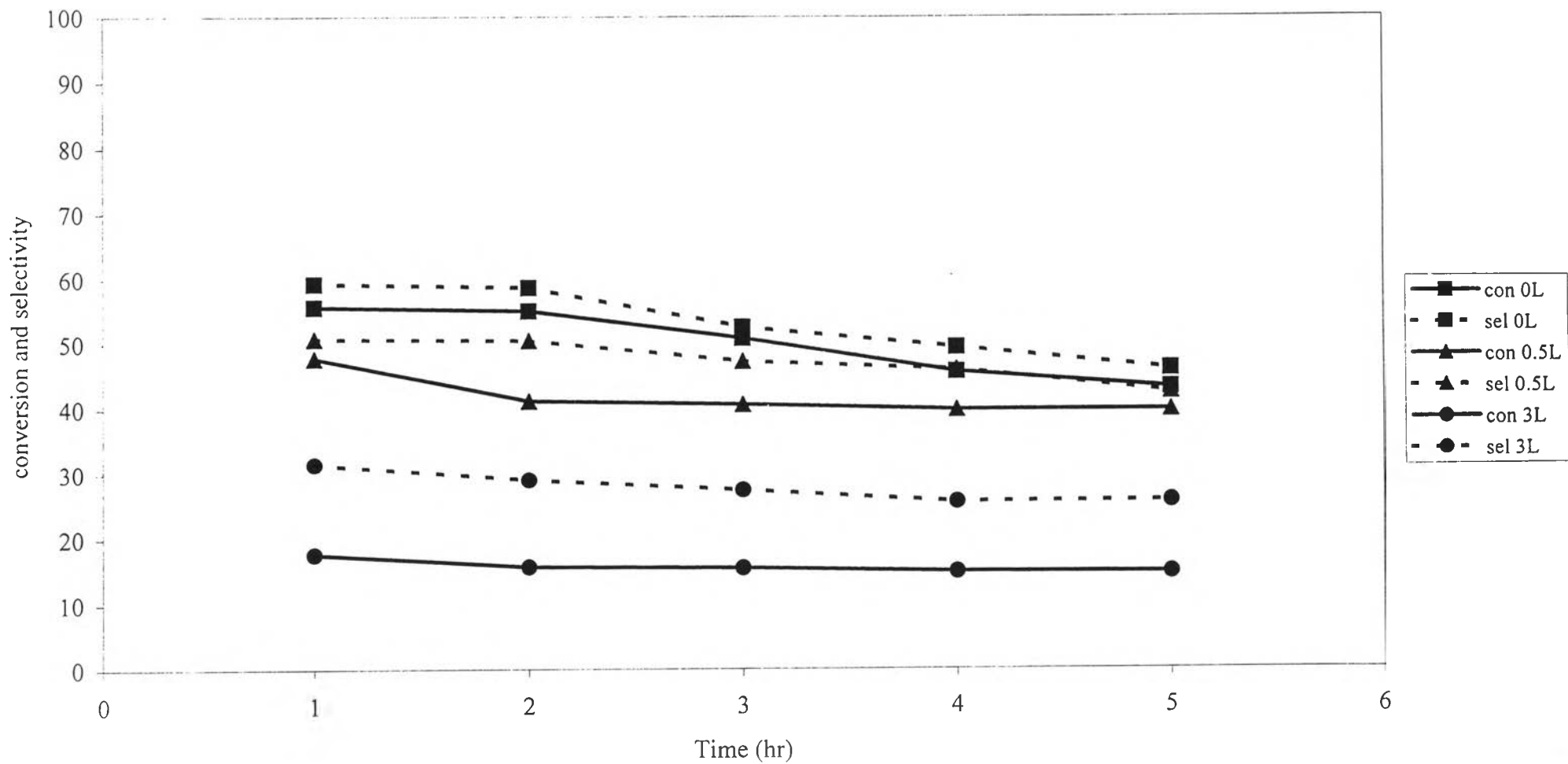


Figure 5.8 Conversion and selectivity with time at 400°C (0L) 2%Pd/SiO₂, (0.5L) 2%Pd/0.5%La₂O₃/SiO₂ and (3L) 2%Pd/3%La₂O₃/SiO₂.

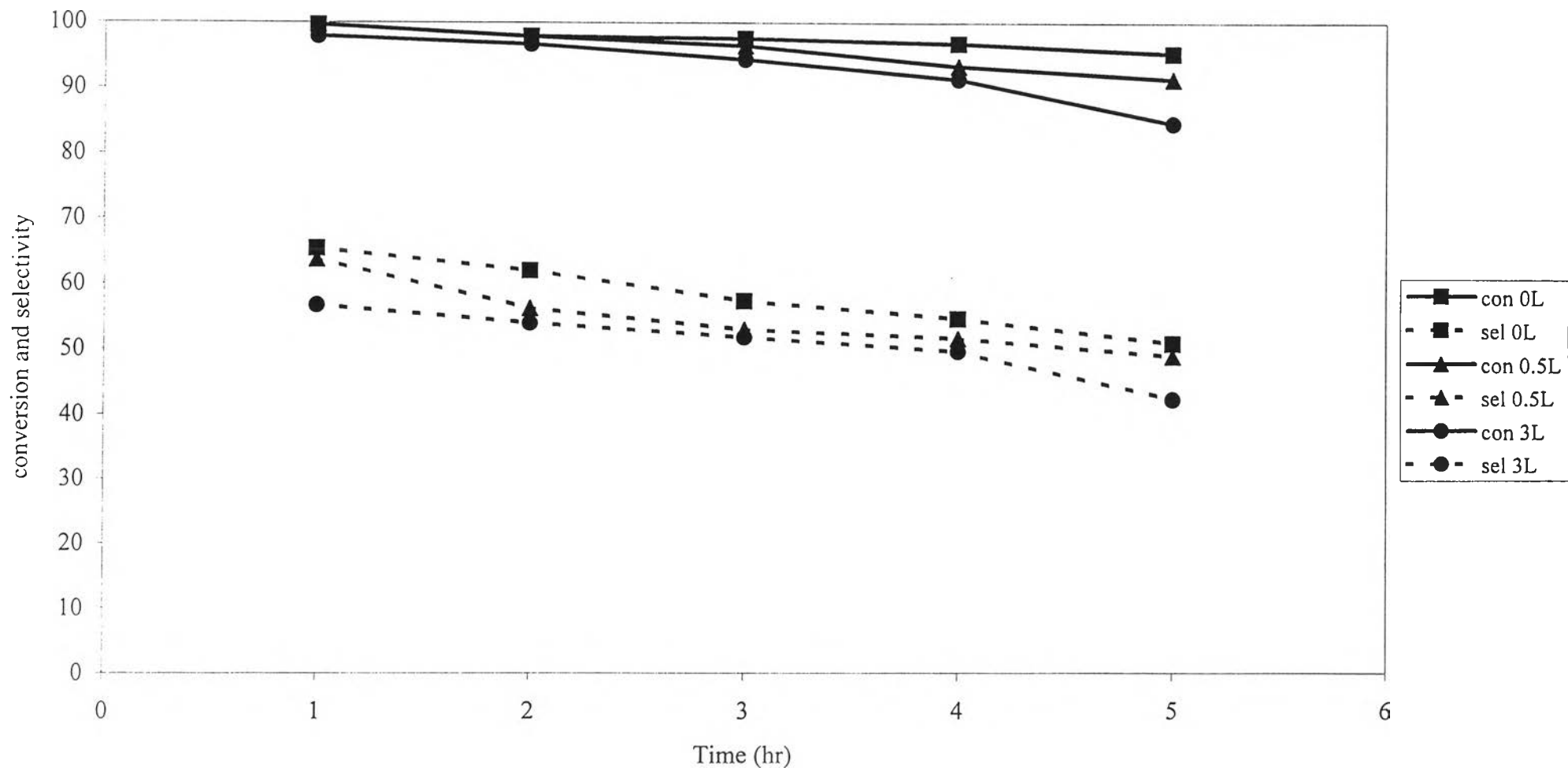


Figure 5.9 Conversion and selectivity with time at 500°C (0L) 2%Pd/SiO₂, (0.5L) 2%Pd/0.5%La₂O₃/SiO₂ and (3L) 2%Pd/3%La₂O₃/SiO₂.

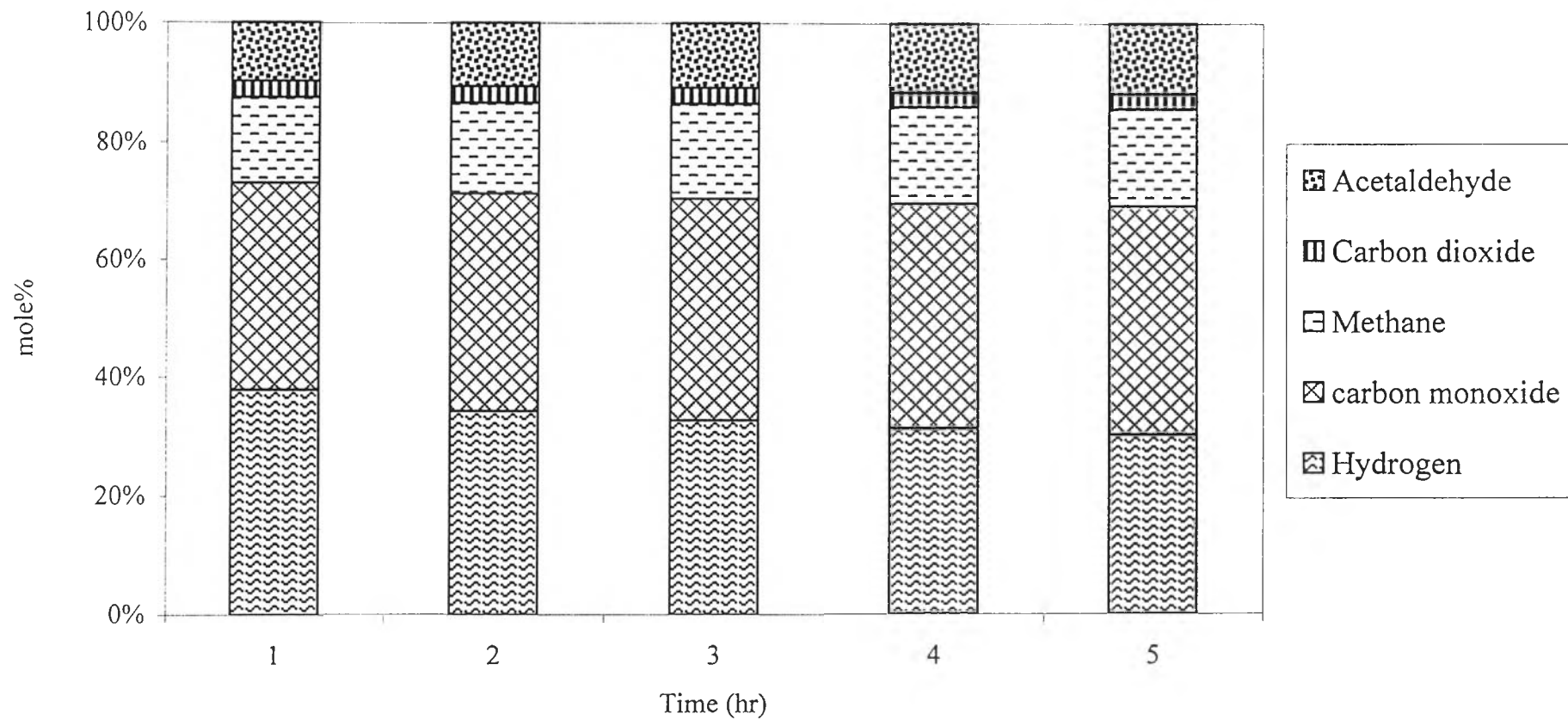


Figure 5.10 Product distribution of 2%Pd/SiO₂ at 200°C.

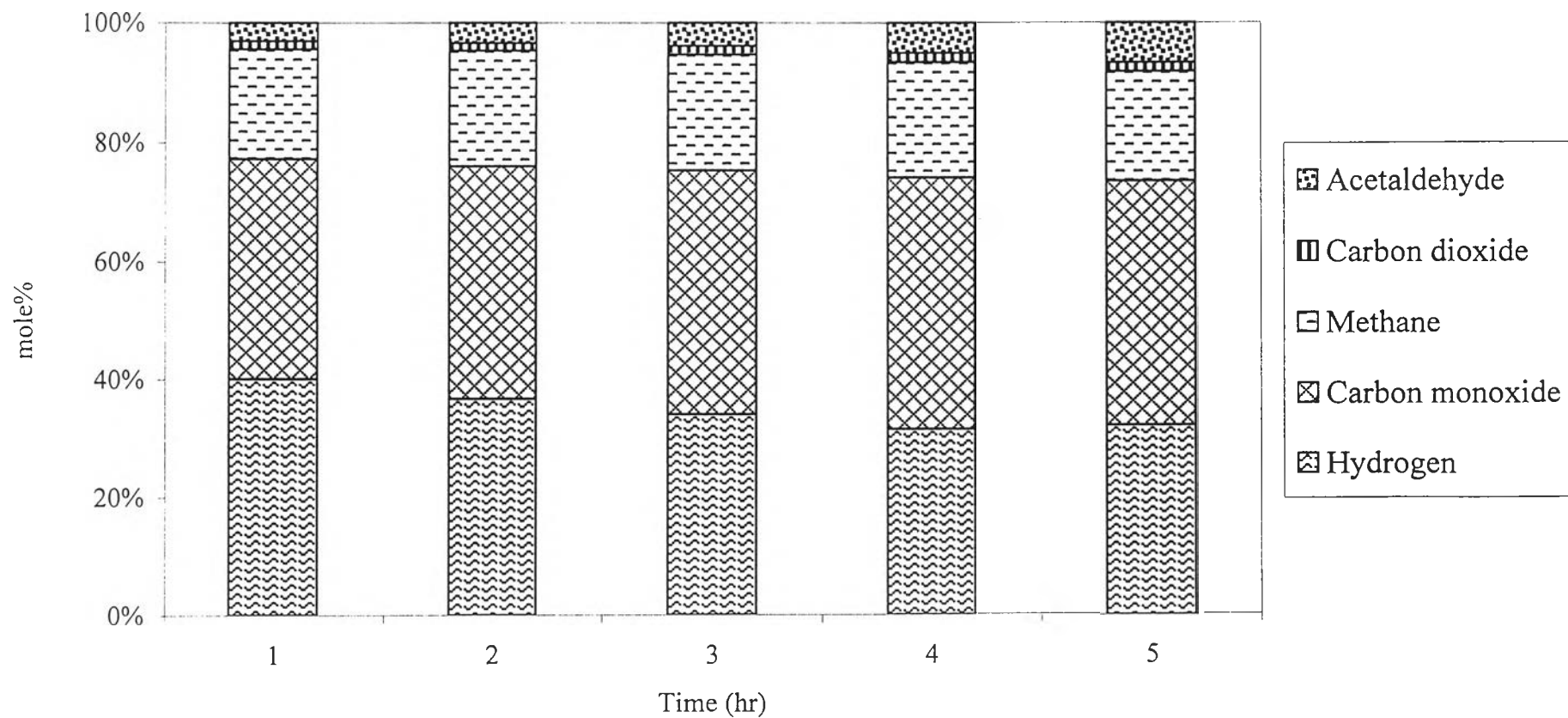


Figure 5.11 Product distribution of 2%Pd/0.5%La₂O₃/SiO₂ at 200°C.

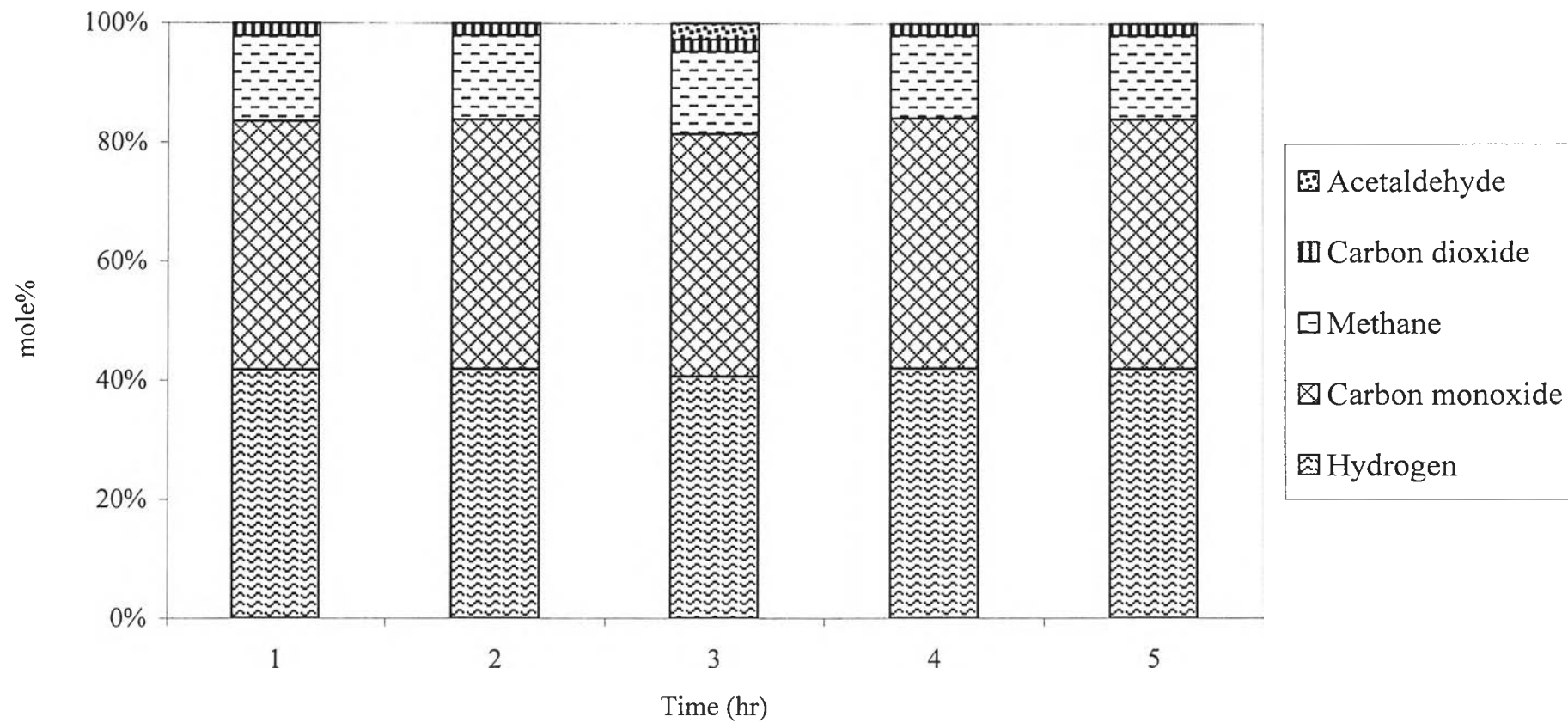


Figure 5.12 Product distribution of 2%Pd/3%La₂O₃/SiO₂ at 200°C.

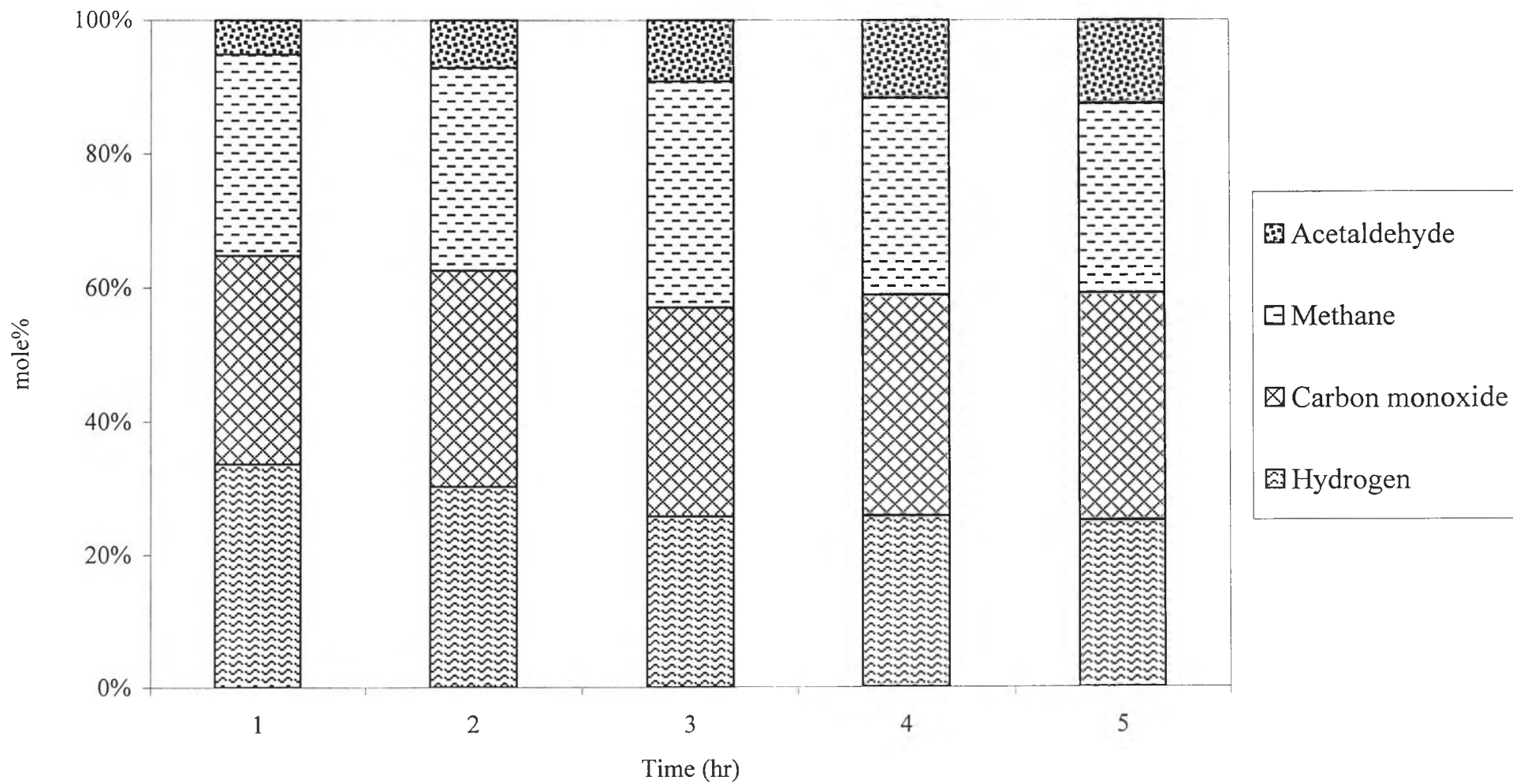


Figure 5.13 Product distribution of 2%Pd/SiO₂ at 300°C.

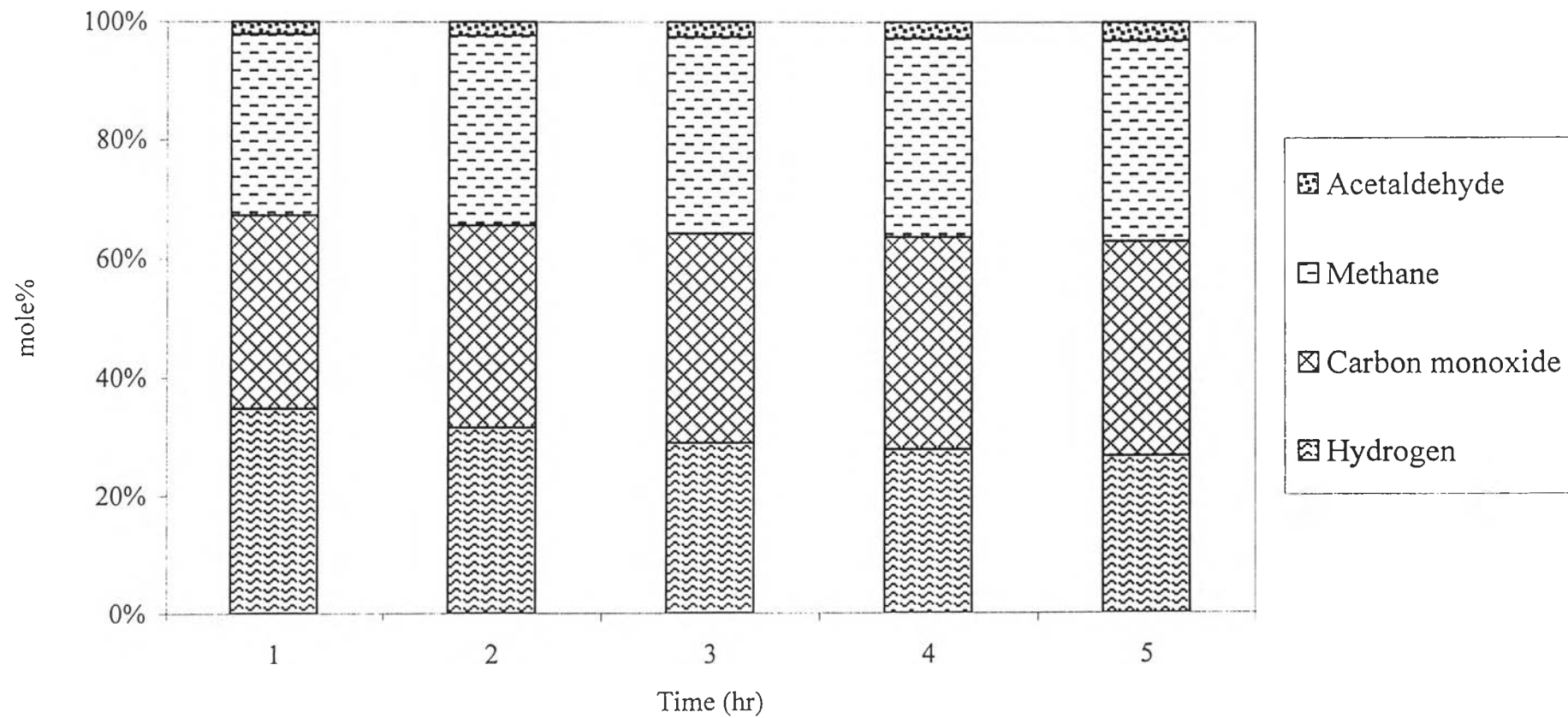


Figure 5.14 Product distribution of 2%Pd/0.5%La₂O₃/SiO₂ at 300°C.

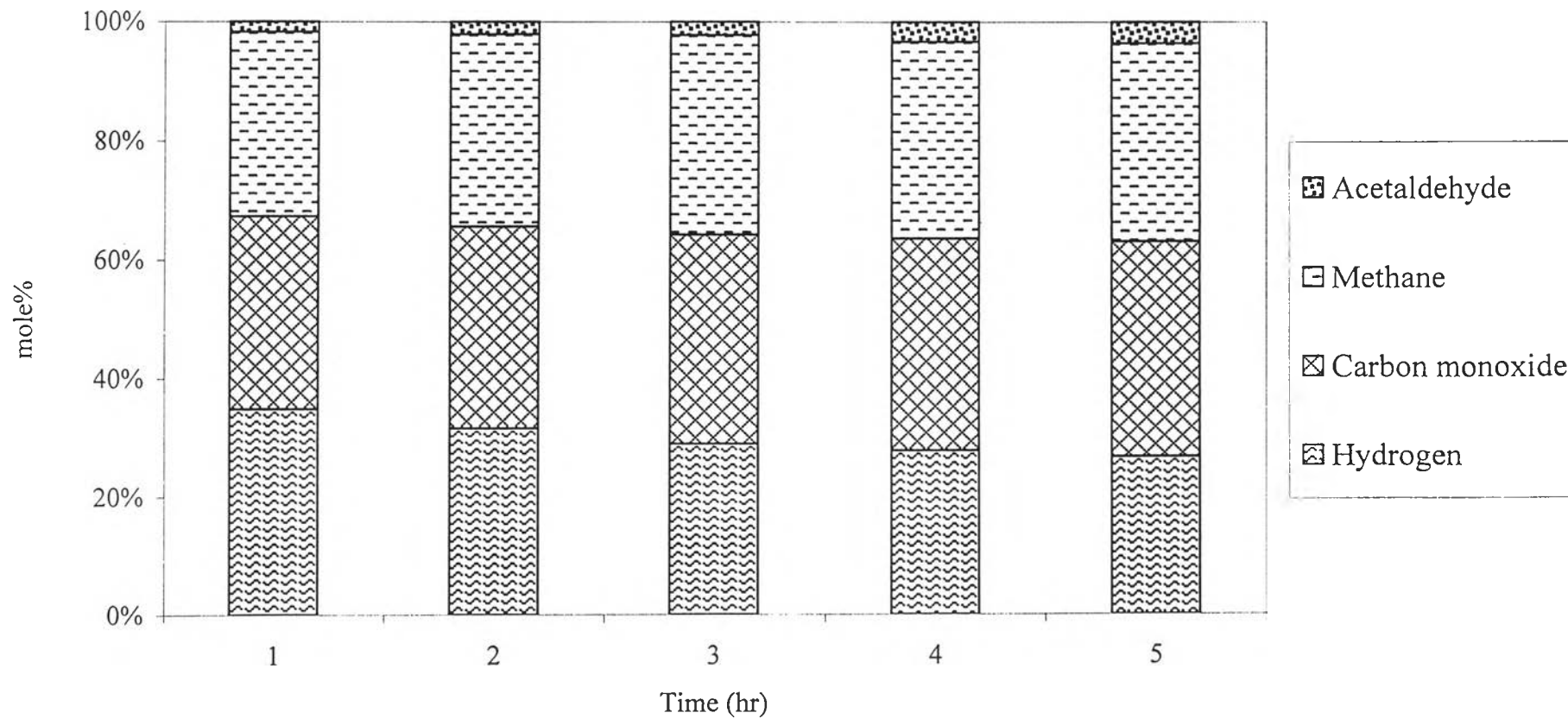


Figure 5.15 Product distribution of 2%Pd/3%La₂O₃/SiO₂ at 300°C.

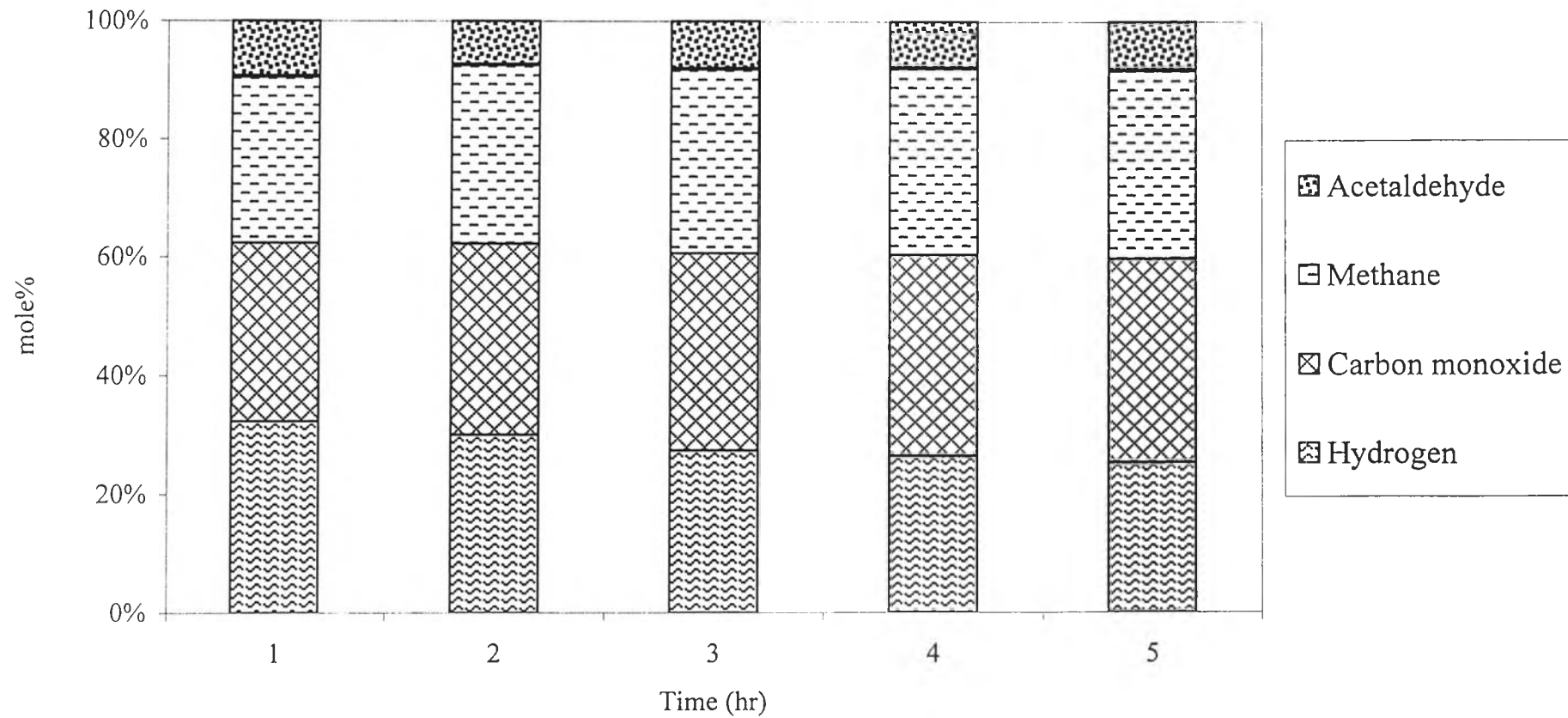


Figure 5.16 Product distribution of 2%Pd/SiO₂ at 400°C.

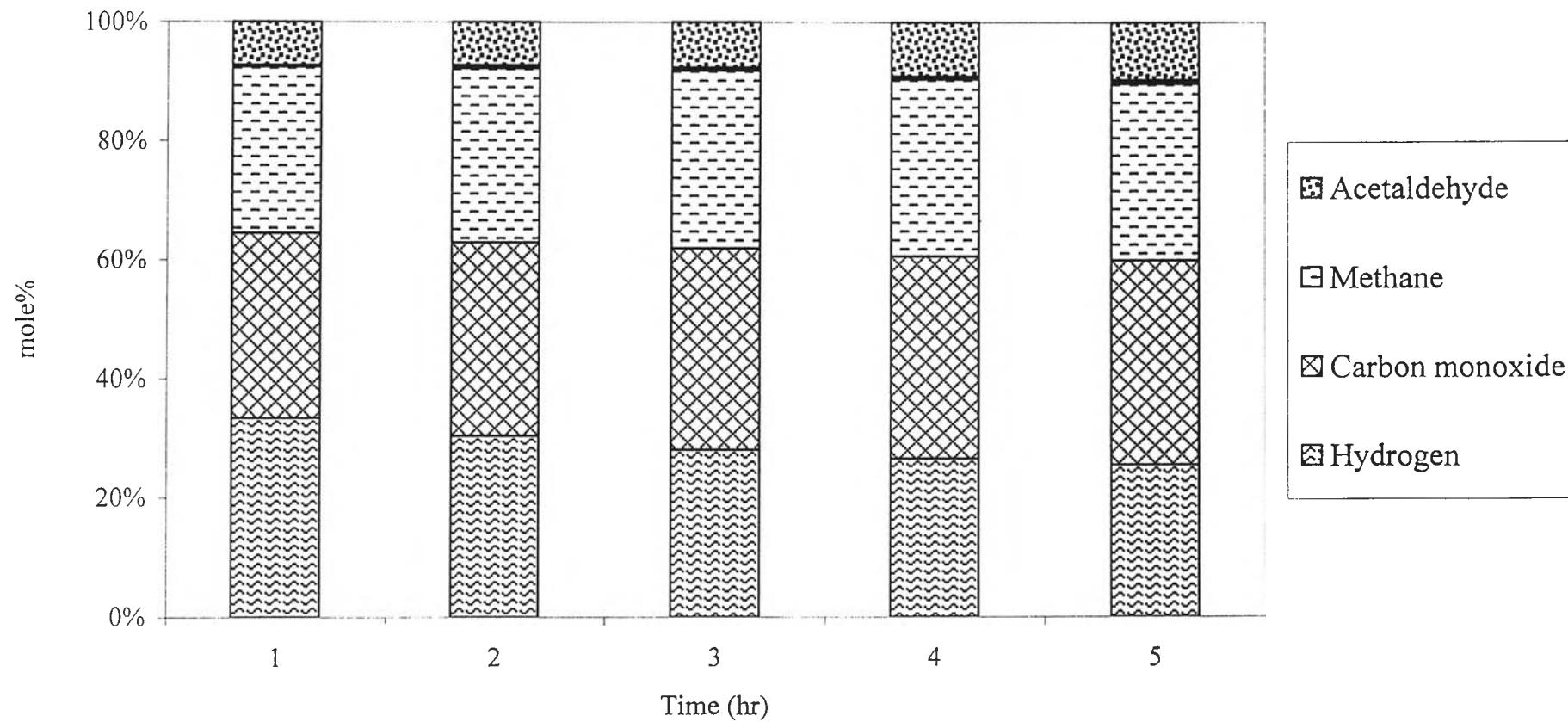


Figure 5.17 Product distribution of 2%Pd/0.5%La₂O₃/SiO₂ at 400°C.

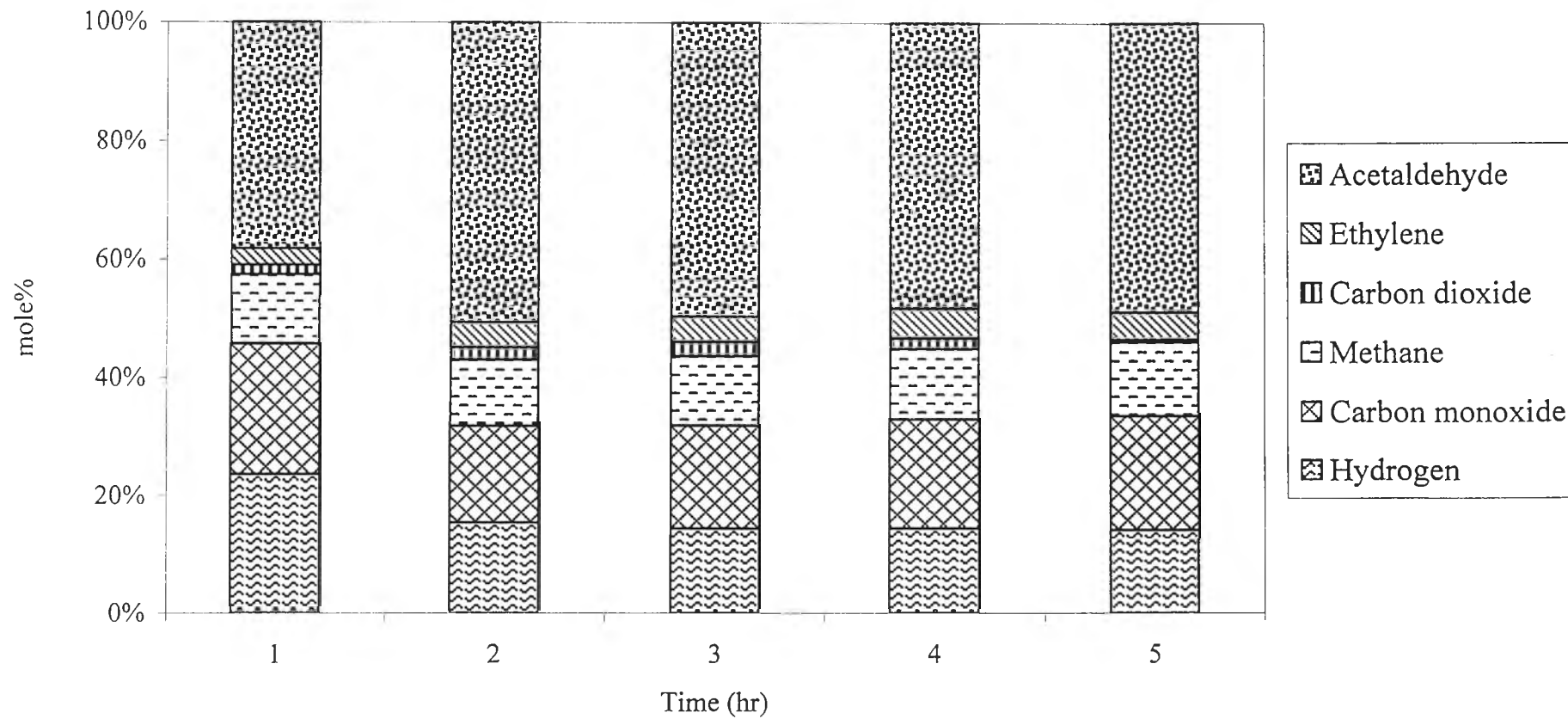


Figure 5.18 Product distribution of 2%Pd/3%La₂O₃/SiO₂ at 400°C.

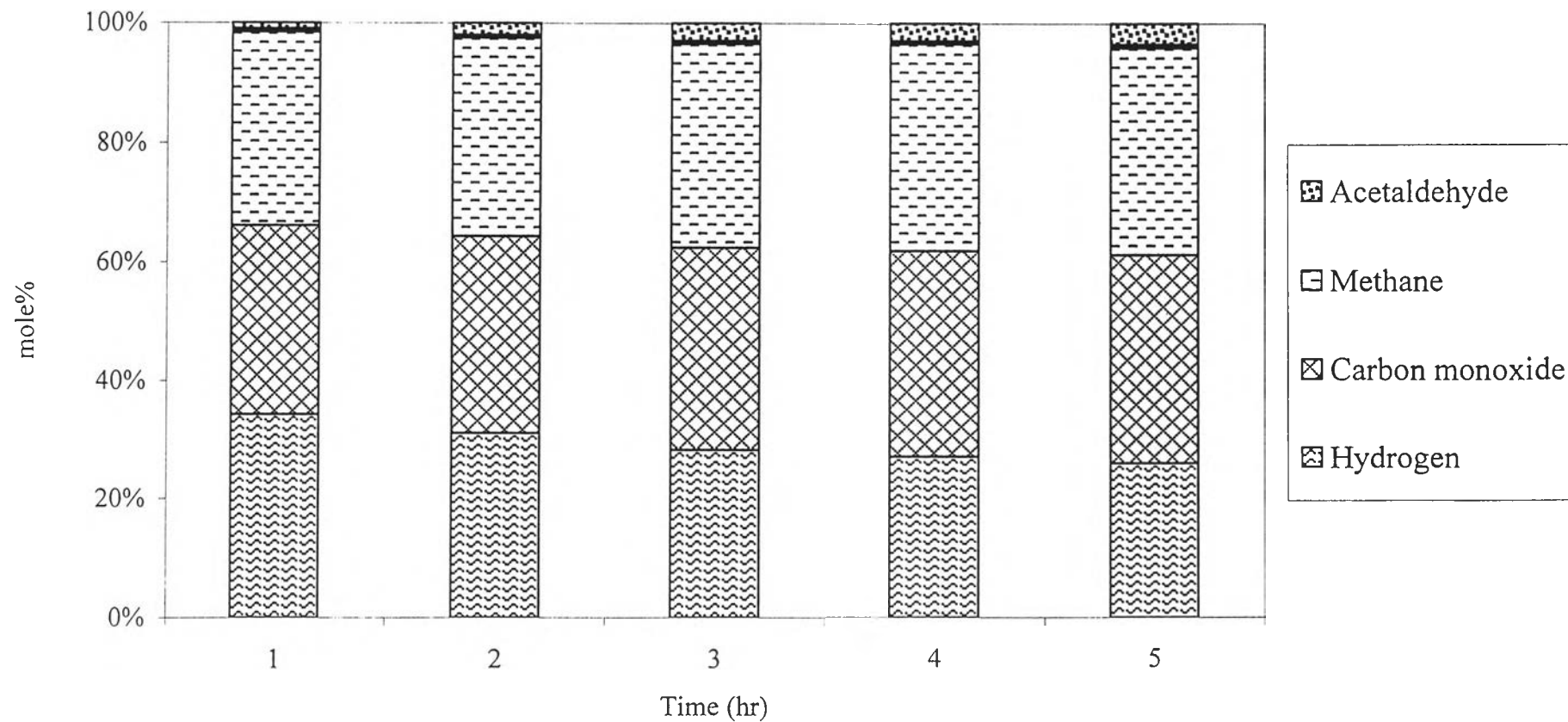


Figure 5.19 Product distribution of 2%Pd/SiO₂ at 500°C.

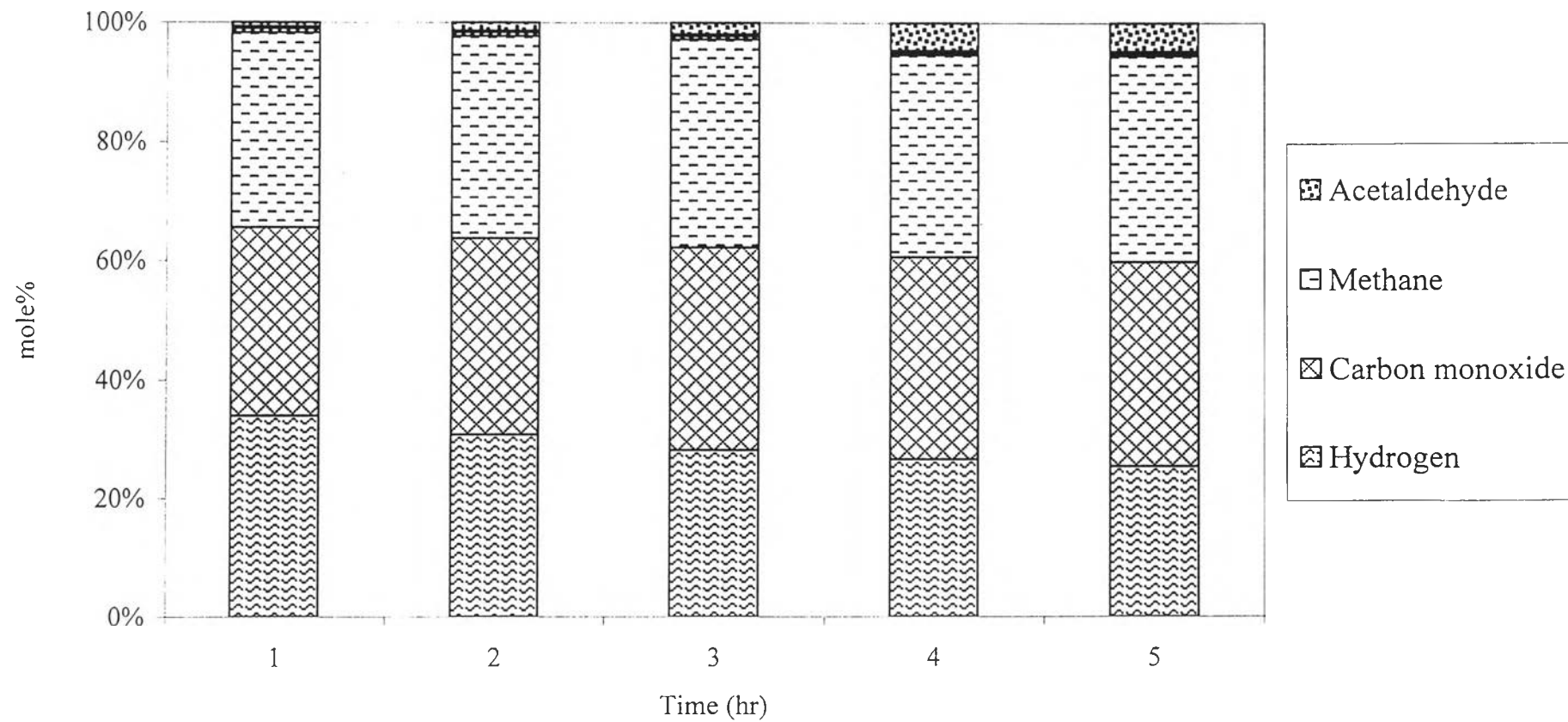


Figure 5.20 Product distribution of 2%Pd/0.5%La₂O₃/SiO₂ at 500°C.

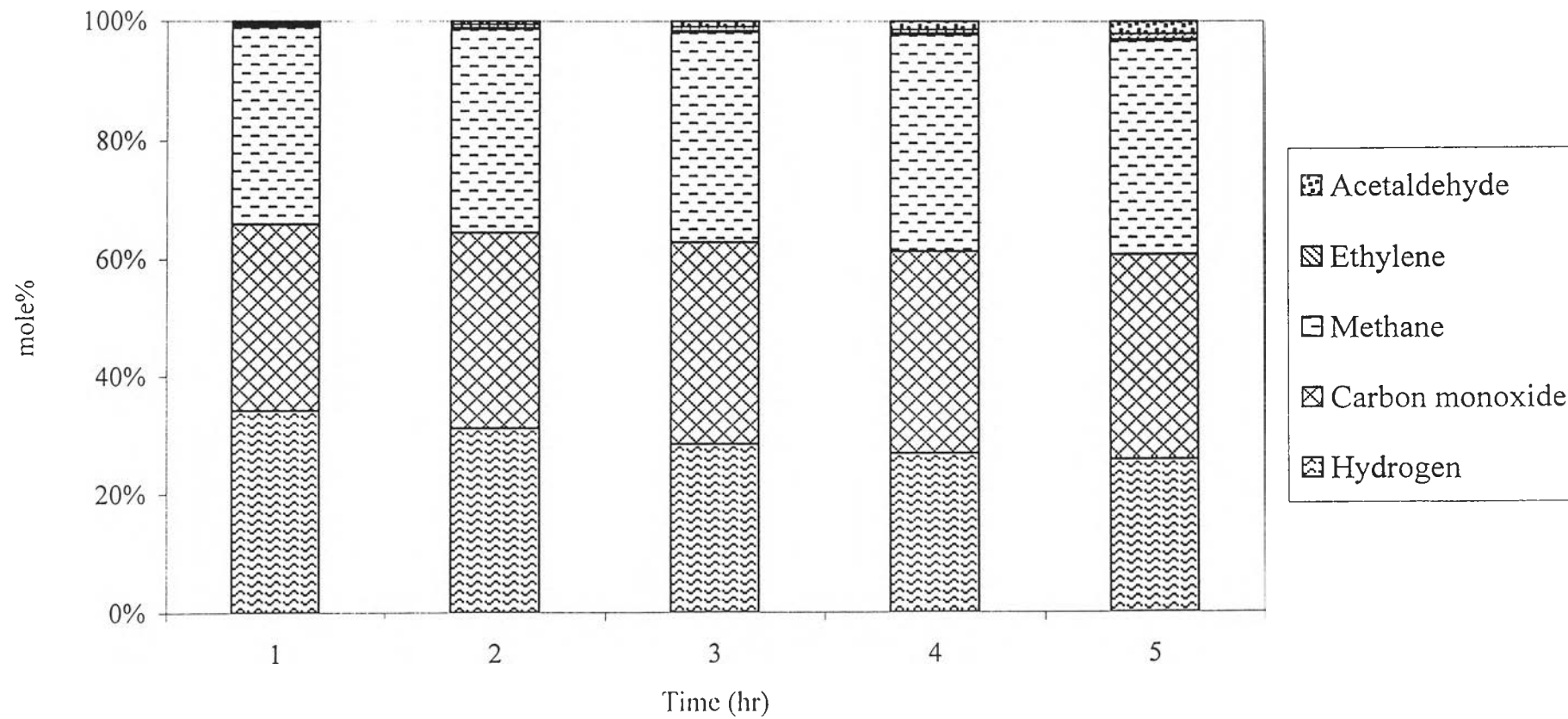


Figure 5.21 Product distribution of 2%Pd/3%La₂O₃/SiO₂ at 500°C.

5.3 Catalyst deactivation by coking

An important feature of catalytic decomposition of ethanol is that the catalyst deactivates in the course of the process as presented in Figures 5.6-5.9. The main cause of the deactivation is the deposition of coke on the active site of metal, producing a lowering of the activity and selectivity. The ethanol decomposition was carried out for 5 hr in the temperature range 200-500°C in order to investigate whether how severe the catalyst deactivation was. Spent catalysts were characterized by means of TPO technique. The results showed characteristics of coke deposition on catalyst. The pattern of TPO refers to coke location while area under the curve refers to coke amount generated.

There was a study of coke generated over palladium catalysts by Marecot and coworkers [18]. The paper revealed that the spectrum peak at approximate 250°C was attributed to coke deposited on palladium atoms of high coordination number while the peak at approximate 400°C would involve palladium atoms of low coordination number like corners or edges. However, for the peak at approximate 550°C, it corresponds to the coke on the support. Figures 5.22 through 5.25 present the TPO patterns of the set of used catalysts with respect to temperature.

5.3.1 TPO obtained at condition 200°C

TPO patterns resulted from 200°C (see Figure 5.22) condition gave small amount of coke compared to other temperature conditions (the lowest area under the curve). The quantitative analysis pointed that coke deposition over catalyst were 0.69, 0.53, and 0.50 over 2%Pd/SiO₂, 2%Pd/0.5%La₂O₃/SiO₂, and 2%Pd/3%La₂O₃/SiO₂, respectively. It, thus, agreed that the amount of coke deposition was decreased upon lanthana loading. These results were consistent to constant stability of catalysts, a tiny declination of activity and selectivity over 5 hr TOS (see Figure 5.6). Considering a TPO spectra as Figure 5.21, there are two peaks appeared. The first peak appears at 250°C, which refers to coke generated on active

metal site. The second peak appears at 550°C, which refers to coke generated on the acidic site far away from any metal site.

Coke deposited on metal over both lanthana-modified and unmodified catalyst were found to be somewhat same amount of coke. However, coke over support via unmodified catalyst was higher than those via modified catalysts. This means coking rate obtained from unmodified support is higher than that with modified support.

Since the temperature condition does not provide ethanol dehydration to ethylene, the polymerization of ethylene would not be found, as well. Coke appeared from this TPO experiment, then, was not formed through out the polymerization process. However, only one way to generate coke should be via the dissociation of some other intermediates, which was not be clear.

5.3.2 TPO obtained at condition 300°C

At the temperature condition of 300°C (see Figure 5.23), TPO patterns after this condition obtained a little bigger than those after condition 200°C. Coke depositions were 1.3, 0.86, and 0.57 over 2%Pd/SiO₂, 2%Pd/0.5%La₂O₃/SiO₂, and 2%Pd/3%La₂O₃/SiO₂, respectively. Like those results obtained from 200°C, the amounts of coke deposition were decreased upon higher lanthana loading. The results again were consistent to the constant stability of lanthana-modified catalysts (see Figure 5.7). Considering their TPO patterns, they are identified as 2 peaks. The first peak appears at 250°C, which refers to coke generated on active metal site. The second peak appears at 550°C, which refers to coke generated on the acidic site far away from any metal site.

5.3.3 TPO obtained at condition 400°C

The TPO patterns of spent catalysts obtained after operating at 400°C are presented in Figure 5.24. There are 2 peaks appear similar to those other conditions (200,300°C). Therefore, the locations of coke deposition could be what already was

discussed. However, the peak heights showed should be taken into a consideration. It was found that peak height and area underneath the curve at 250°C obtained from 2%Pd/SiO₂ was lower than those from other modified supports. It was found that the higher lanthana loading, the higher area under the curves was. This results correspond to the higher active sites over lanthana-modified catalysts. The metal size must be bigger than the critical size of coke. The carbon deposition were found to be 2.71, 5.59, and 2.37 over 2%Pd/SiO₂, 2%Pd/0.5%La₂O₃/SiO₂, and 2%Pd/3%La₂O₃/SiO₂, respectively. Lanthana still inhibits the total coke deposit, but it also assists the accumulation of coke over metal sites via promoting the polymerization of ethylene.

5.3.4 TPO obtained at condition 500°C

The TPO patterns of spent catalysts over 500°C are illustrated in Figure 5.25. It is obvious that the accumulation of coke was higher than that obtained from lower temperature condition. Consider the TPO pattern, it is found that they were different from those at lower temperature condition. TPO pattern contains 3 peaks. The first peak is about 250°C, second peak is around 550°C and last peak nearly 700°C. The first peak attributes to coke deposits on metal sites while the second one refers to carbonaceous deposits on acidic sites at the edge. The peak appeared at 700°C might refer to coke developed from coke at 550°C. Coke required high temperature (700°C) to remove possibly refers to well arranged-structure. The carbon deposition on catalyst is 8.19, 7.21, and 15.71 over 2%Pd/SiO₂, 2%Pd/0.5%La₂O₃/SiO₂, and 2%Pd/3%La₂O₃/SiO₂, respectively. The high amount of coke at this temperature came from low selectivity and high conversion.

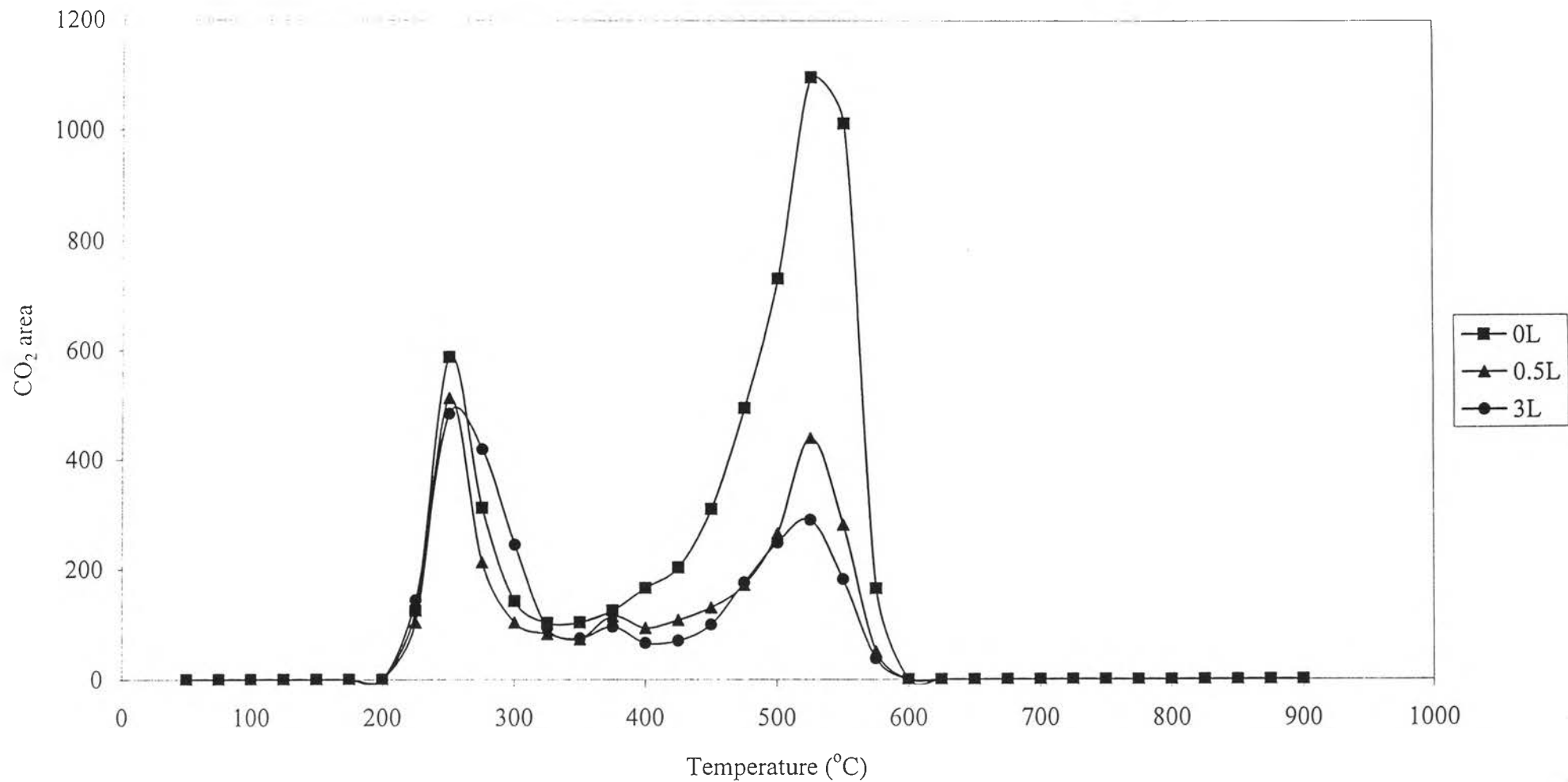


Figure 5.22 TPO curve of 200°C (0L) 2%Pd/SiO₂, (0.5L) 2%Pd/0.5%La₂O₃/SiO₂ and (3L) 2%Pd/3%La₂O₃/SiO₂.

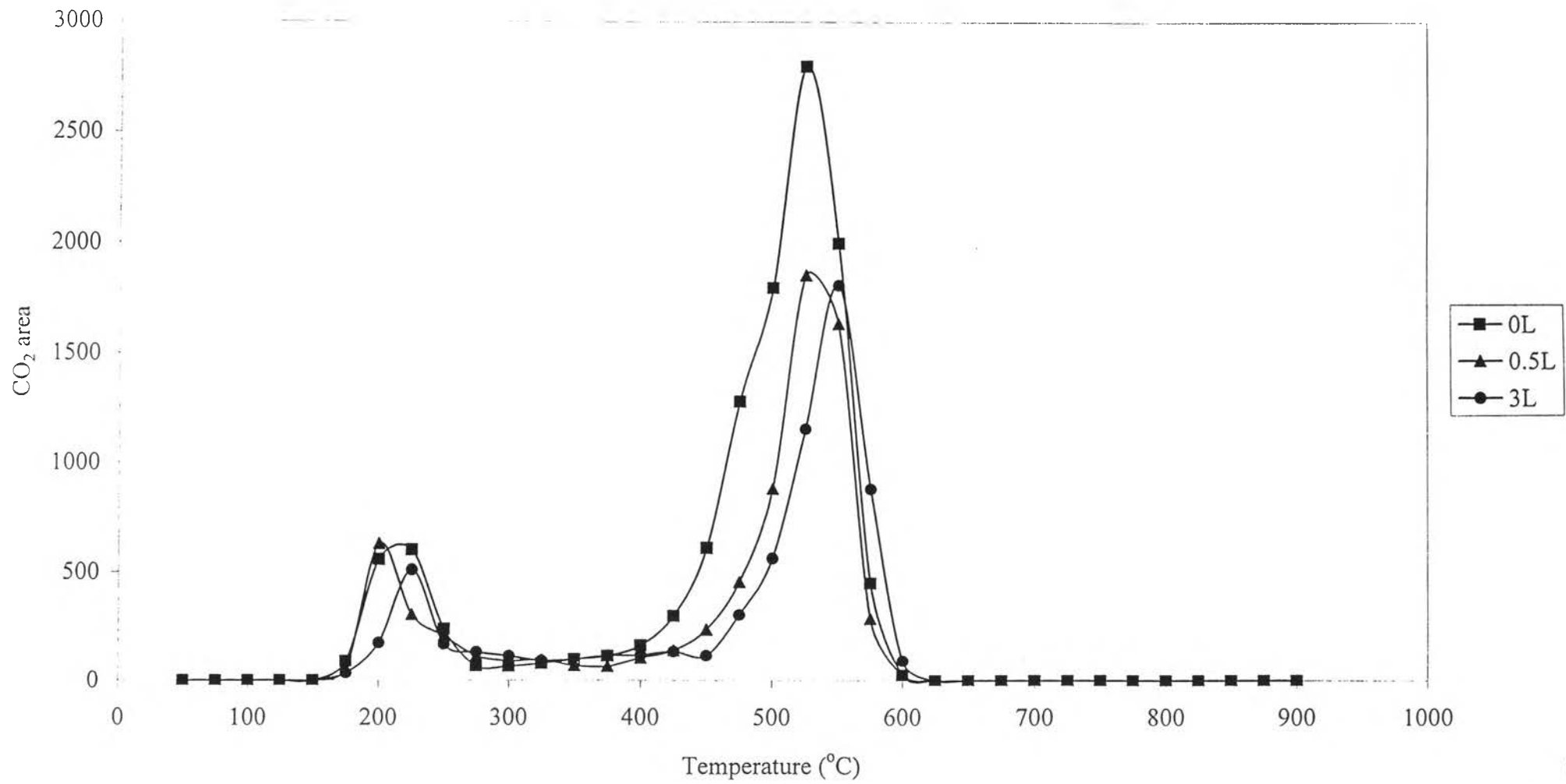


Figure 5.23 TPO curve of 300°C (0L) 2%Pd/SiO₂, (0.5L) 2%Pd/0.5%La₂O₃/SiO₂ and (3L) 2%Pd/3%La₂O₃/SiO₂.

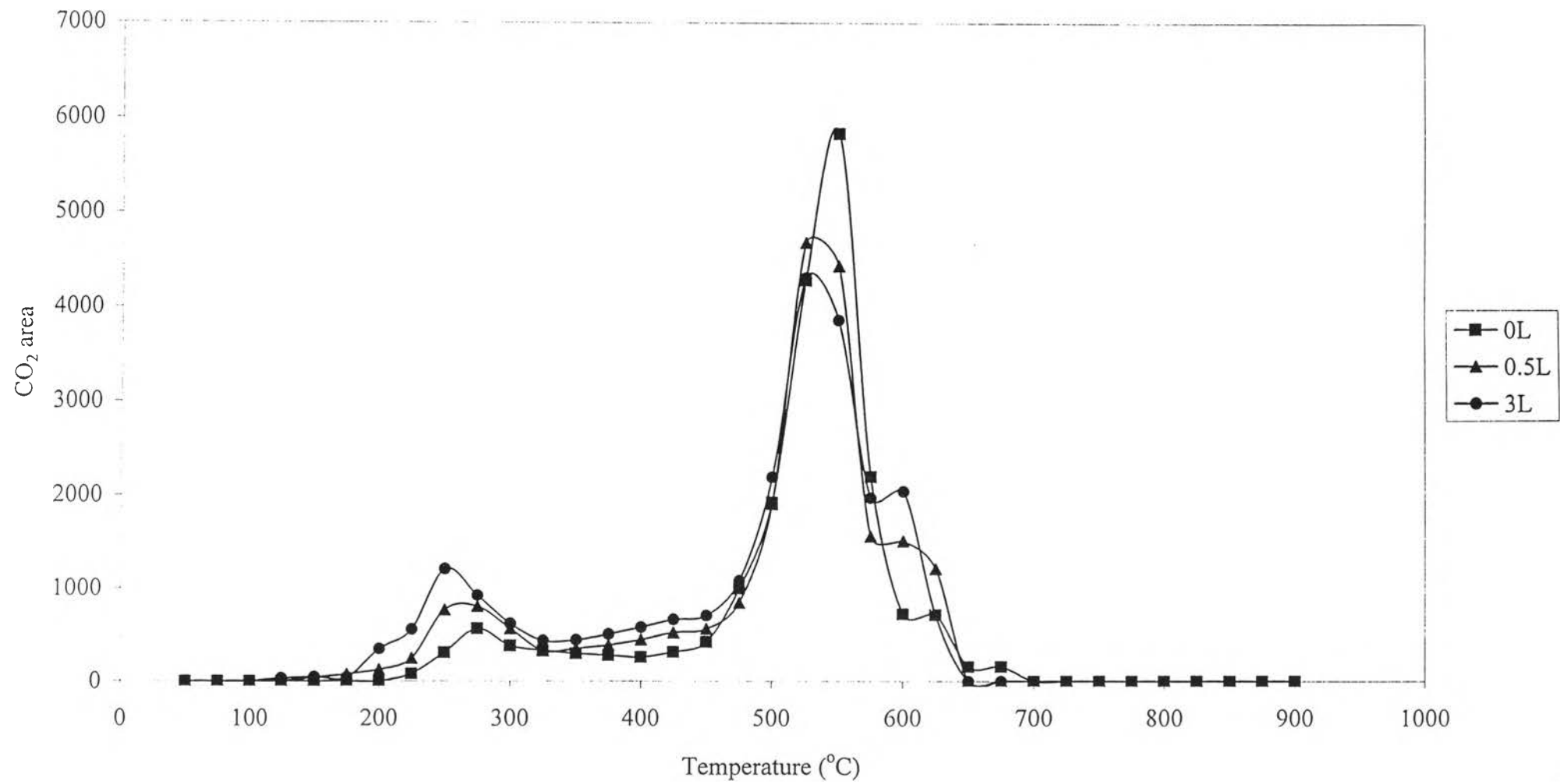


Figure 5.24 TPO curve of 400°C (0L) 2%Pd/SiO₂, (0.5L) 2%Pd/0.5%La₂O₃/SiO₂ and (3L) 2%Pd/3%La₂O₃/SiO₂.

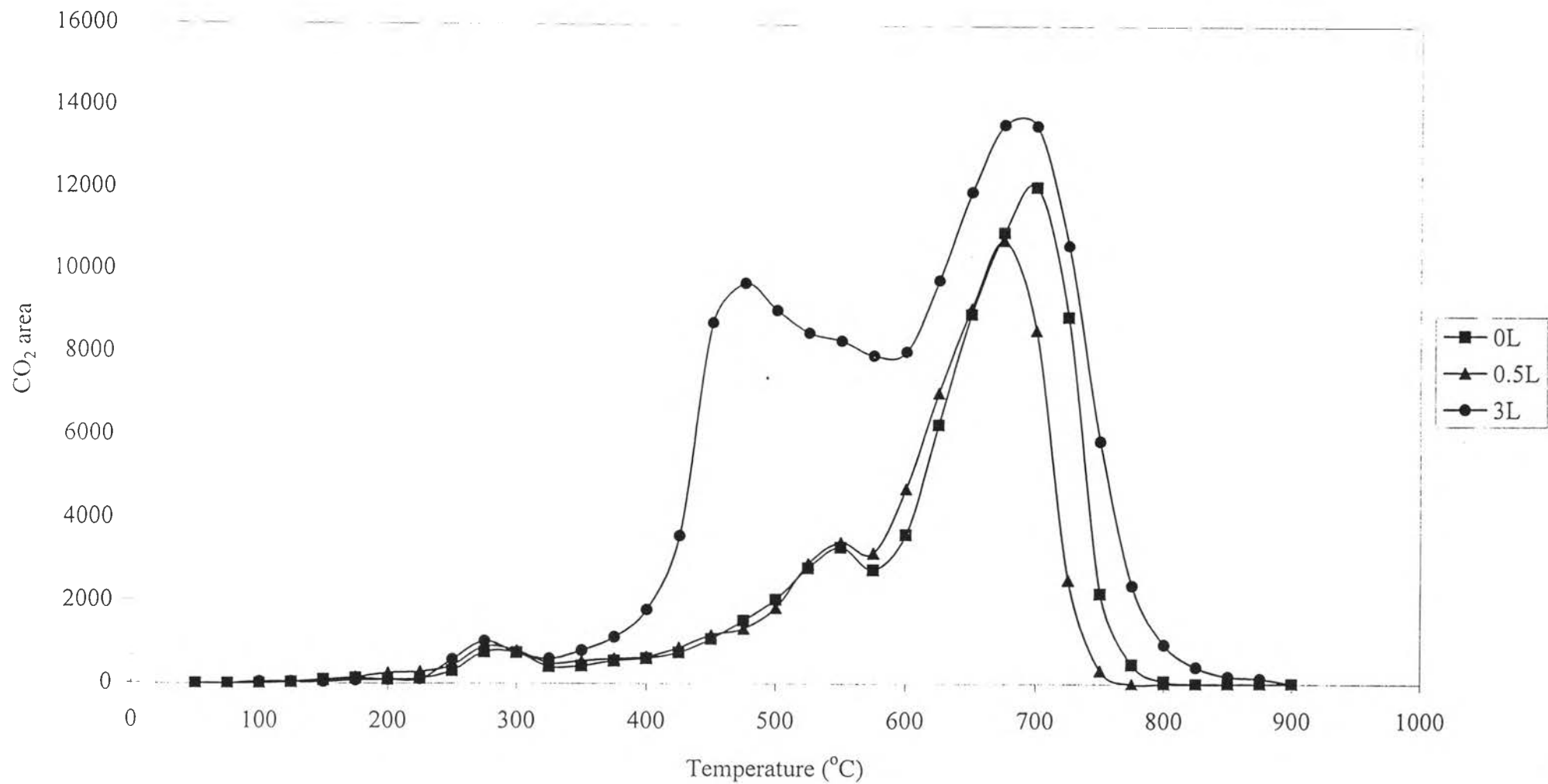


Figure 5.25 TPO curve of 500°C (0L) 2%Pd/SiO₂, (0.5L) 2%Pd/0.5%La₂O₃/SiO₂ and (3L) 2%Pd/3%La₂O₃/SiO₂.