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Activation of acetylene selective hydrogenation catalysts using oxygen containing compounds

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Abstract

Hydrogenation of acetylene in the presence of a large excess of ethylene has been investigated on the Pd–Ag catalyst at 60°C with a space velocity of 2000 h^{-1}. It was found that an enhancement in the performance of Pd–Ag catalyst can be obtained by pretreatment with N_2O. It is suggested that a certain amount of N_2O added to the catalyst before use not only augments the sites associated with ethylene production from acetylene, but also depletes the sites responsible for direct ethane formation. Upon aging, the pretreated catalyst exhibited good stability. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Selective hydrogenation; Acetylene; Silver promoted palladium catalyst; N_2O pretreatment

1. Introduction

The selective hydrogenation of acetylene over supported palladium catalysts is a widely used process to purify the ethylene produced by steam cracking of hydrocarbons. The ethylene to acetylene ratio in the stream to be treated is generally higher than 70 [1]. Typically the acetylene concentration can be reduced from an initial value in the region of 5000 to below 5 ppm with hydrogenation of not more than 1% of the ethylene, operating at temperatures in the range of about 60–70°C [2]. At present all such catalysts are based on palladium using alumina as support, and palladium-based catalysts promoted by a second metal are now available [3]. The promoter improves selectivity or stability of the catalyst. Sarkany et al. [4] have clearly demonstrated that the addition of copper to palladium causes a significant decrease in the overall rate of ethane formation and at the same time there is a decrease in the catalyst activity as well as a marginal decrease in oligomer selectivity. Recently, it has been discovered that the catalyst comprising elements of group IB and transition metals could be activated with N_2O before use [5]. Thus it is an objective of the study to pretreat the Pd–Ag catalyst before being used for the selective hydrogenation of acetylene.

2. Experimental

A 0.04 wt.% Pd–Ag/γAl_2O_3 (Ag : Pd = 4 : 1) was prepared via the serial impregnation method. Alumina support was impregnated with palladium first followed by silver. Alumina support was Al_2O_3 (CS-303) supplied by United Catalyst Incorporation (UCI), USA. Palladium nitrate and silver nitrate were used as sources for Pd and Ag, respectively. The calcination temperatures for palladium and silver were 300 and 370°C, respectively.

A portion of 0.2 g of the catalyst was packed into a 0.6 cm ID quartz reactor and heated from room temperature to 100°C in Ar. When the temperature reached 100°C, the reduction was made by switching

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Ar to H_2 and maintained at that temperature for 2 h. After reduction, H_2 was purged with a flow of Ar while the reactor was cooled down to 60°C and held at that temperature for 10 min. Then a gas mixture of 0.3% C_2H_2, 0.8% H_2 and C_2H_4 balanced was switched to replace Ar with a flow rate of 30 ml/min. Consequently, the gas mixture was reacted under catalytic hydrogenation, i.e., C_2H_2 was selectively hydrogenated to C_2H_4. However, in the case of N_2O treatment, the reactor was cooled down from 100 to 90°C under Ar flow and held for 10 min before N_2O injection. Then the temperature was reduced to 60°C and the reaction was started. The products were analyzed by Shimadzu FID GC 14B equipped with Carbosieve column s-2.

To investigate the effect of carbonaceous deposit on the catalysts, the following experiment was designed: set A was obtained at an early period (5 min on stream) during which the negligible amount of coke was formed, while set B was obtained at 44 h on stream during which the considerable amount of coke was presumably formed though the exact amount of coke deposit was not determined.

The active sites of the catalysts were determined by CO adsorption technique and the BET surface areas by a Micromeritic Surface Area Analyzer (model ASAP 2000).

The following terms used herein are defined as:

$$\text{Acetylene conversion (\%)} = \frac{\text{acetylene in feed} - \text{acetylene in product}}{\text{acetylene in feed}} \times 100$$

$$\text{Ethylene selectivity (\%)} = \frac{\text{ethylene in product} - \text{ethylene in feed}}{\text{acetylene converted}} \times 100$$

$$\text{Yield per pass (YPP)} = (\text{\% of acetylene conversion}) \times (\text{\% of ethylene selectivity})$$

3. Results and discussion

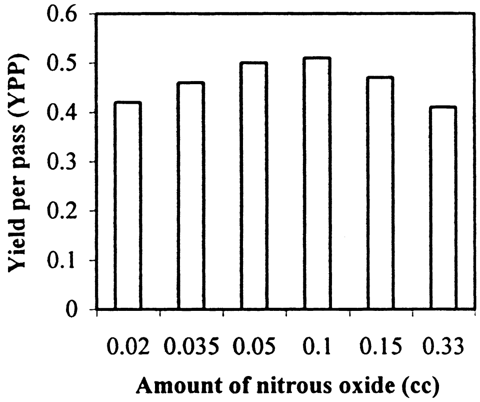

Fig. 1. Performance of 0.04 wt.% Pd–Ag/Al_2O_3 (Ag : Pd = 4 : 1) versus the amount of nitrous oxide addition ranging from 0.02 to 0.33 cm^3. Reaction conditions: 60°C, GHSV 2000 h^{-1}, 5 min on stream.

Fig. 1 shows the effect of N_2O addition on the performance of 0.04 wt.% Pd–Ag/Al_2O_3 (Ag : Pd = 4 : 1). Addition of 0.02–0.1 cm^3 of N_2O markedly increased the YPP of ethylene. The best result was obtained with 0.1 cm^3 injection of N_2O while the YPP declined with the amount of N_2O higher than 0.1 cm^3. It has been suggested that N_2O addition may cause the formation of both silver oxide and palladium oxide on the surface of Al_2O_3 support [5]. The formation of silver oxide should increase the number of accessible Pd active sites, as shown in Fig. 2, thus promoting the hydrogenation of acetylene to ethylene. The oxidation of active Pd to palladium oxide, however, may possibly cause the loss of active sites also. The maximum YPP of ethylene obtained with 0.1 cm^3 injection of N_2O may be attributed to the simultaneous reproduction and destruction of active sites in which the former is more predominant, particularly the sites responsible for ethylene production from acetylene.

Figs. 3 and 4 show the effect of catalyst aging on acetylene conversion and ethylene selectivity, respectively, for 0.04 wt.% Pd–Ag/Al_2O_3 with and without N_2O treatment. It has been found that both catalysts exhibited similar results in decreasing ethylene selectivity with time on stream, while acetylene conversion was only slightly changed. After 60 h of operation, both catalysts attained an apparent steady state of ethylene selectivity. It has been clearly observed that the N_2O-treated catalyst exerted higher activity and selectivity than the untreated one.

From several previous investigations (Al-Ammar and Webb [6–8], Margitfalvi et al. [9,10], Moses et al. [11], and Weiss et al. [12]), it has been generally

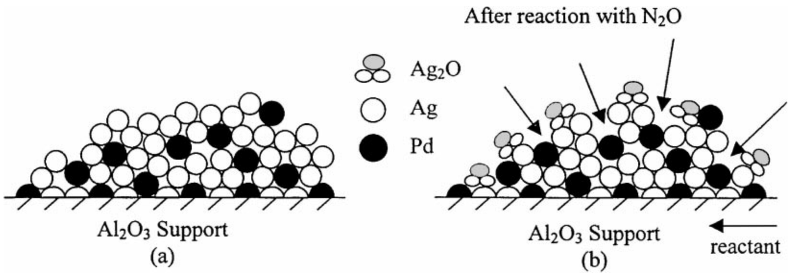

Fig. 2. Proposed model illustrating the effect of N_2O addition on enhancing the accessible sites of active Pd responsible for acetylene hydrogenation to ethylene.

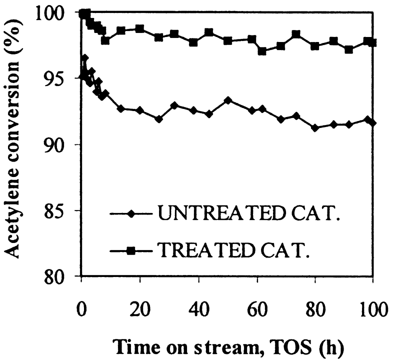

Fig. 3. Effect of catalyst aging on acetylene conversion over untreated and N_2O-treated Pd–Ag/Al_2O_3. Reaction conditions: 60°C, GHSV 2000 h^{-1}.

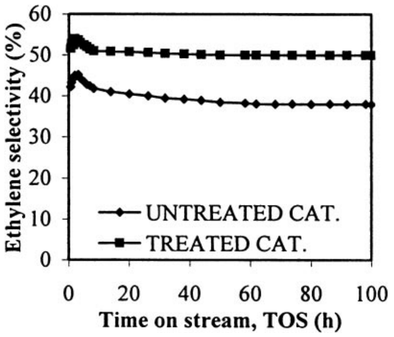

Fig. 4. Effect of catalyst aging on ethylene selectivity over untreated and N_2O-treated Pd–Ag/Al_2O_3. Reaction conditions: 60°C, GHSV 2000 h^{-1}.

accepted that four main types of surface sites are involved in the alumina-supported Pd catalyst. Fig. 5 illustrates four main types of surface sites; three types of which located on the Pd metal surface, are responsible for selective conversion of acetylene to ethylene, direct ethane production from acetylene, and oligomer formation from acetylene. Another site located on the alumina support surface involves the hydrogenation of ethylene to ethane. It has been reported from some researchers [3,13] that the decrease in ethylene selectivity (i.e. increase in ethylene hydrogenation) during aging has been related to the amount of carbonaceous adsorbate on the catalyst surface. In other words, the carbonaceous deposit acts as a hydrogen bridge for the hydrogen spillover from Pd to support.

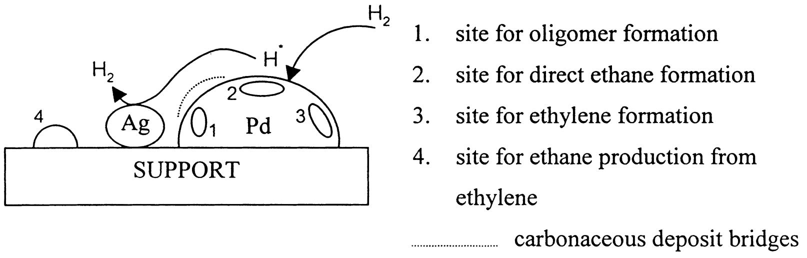

Fig. 5. Conceptual model demonstrating four main types of surface sites on Al_2O_3-supported Pd catalyst and the role of Ag promoter as desorption site for transferred H_2.

Table 1
Product distribution in C wt.% of three kinds of catalysts. Reaction conditions: 60°C, GHSV 2000 h^{-1}

Set	Catalyst	TOS	Composition of the product (%)				C_2H_2 conversion (%)	C_2H_4 selectivity (%)
			C_2H_2 (feed: 0.2099)	C_2H_4 (feed: 99.7708)	C_2H_6 (feed: 0.0121)	CH_4 (feed: 0.0072)		
A	Base[a]	5 min	0.0037	99.8568	0.1321	0.0074	98.23	41.71
	Untreated[b]		0.0065	99.8566	0.1294	0.0074	96.90	42.18
	Treated[c]		0.0015	99.8784	0.1126	0.0073	99.28	51.63
B	Base[a]	44 h	0.0192	99.8338	0.1396	0.0074	90.85	33.04
	Untreated[b]		0.0156	99.8465	0.1305	0.0073	92.56	38.96
	Treated[c]		0.0059	99.8731	0.1134	0.0075	97.18	50.15

[a] 0.04 wt.% Pd/Al_2O_3.
[b] 0.04 wt.% $Pd–Ag/Al_2O_3$.
[c] 0.04 wt.% $Pd–Ag/Al_2O_3$ treated with N_2O.

As shown in Table 1, the substantial amount of ethane obtained for 0.04% Pd/Al_2O_3 of set A should be produced directly from acetylene, and the ethylene hydrogenation to ethane should be negligible with the assumption that no carbonaceous deposit bridge was formed. When the base catalyst was promoted with Ag, the amount of ethane significantly decreased and so did the acetylene conversion while the amount of ethylene was almost constant. This implies that the alumina-supported Pd catalyst promoted by Ag may reduce the sites responsible for direct ethane formation from acetylene which is consistent with the previous investigation [13]. In the case of N_2O treatment for set A, both acetylene conversion and ethylene selectivity markedly increased and the amount of ethane was further decreased. This means that the addition of nitrous oxide augments the sites responsible for ethylene formation from acetylene as described above, and advantageously reduces the sites accounting for direct ethane formation as well. As for set B, the amount of ethylene obtained for 0.04% Pd/Al_2O_3 was considerably less than that of the corresponding catalyst for set A, and so did the acetylene conversion. The carbonaceous deposit on the catalyst surface should be responsible for the decrease in acetylene conversion. It is interesting to note that the amount of ethane formed on the base catalyst for set B was higher than that for set A even with less acetylene conversion. This means that the substantial amount of ethane was formed via the ethylene hydrogenation on the support sites, with aid of carbonaceous deposit acting as H_2 bridge, rather than the direct ethane formation from acetylene on Pd sites. Sarkany [14,15] has found that the hydrocarbonaceous deposit on Pd/Al_2O_3 catalyst may enhance the over-hydrogenation of 1,3-butadiene and permits the hydrogenation of propene in the presence of 1,3-butadiene due to transport hindrance of 1,3-butadiene. Thus, the over-hydrogenation of acetylene and hydrogenation of ethylene in the presence of acetylene can also be interpreted by transfer limitation of acetylene caused by the presence of carbonaceous deposits. With the Ag-promoted catalyst, the increase in amount of ethylene and acetylene conversion was obtained while the amount of ethane declined. This also implies that the ethylene hydrogenation was reduced by Ag promotion, and the direct ethane formation from acetylene on Pd sites covered with carbonaceous deposit was negligible. Thus, it has been suggested that Ag may hinder the hydrogen spillover from the metal surface to alumina support probably by providing the desorption sites for transferred hydrogen as illustrated in Fig. 5. With the N_2O treatment, both acetylene conversion and ethylene selectivity significantly increased while the amount of ethane was further decreased as similar to those obtained for set A. The improved results achieved on N_2O-treated $Pd–Ag/Al_2O_3$ catalyst for both sets of data essentially contend that the addition of N_2O increases the sites responsible for ethylene formation from acetylene and decreases the sites involving direct ethane formation as mentioned above. Table 2 shows the results of BET surface area of the catalysts. It has been found that the BET surface area of the

Table 2
BET surface area of three catalysts

Catalyst	BET (m^2/g)
0.04 wt.% Pd/Al_2O_3	4.74
0.04 wt.% $Pd–Ag/Al_2O_3$ (untreated)	4.36
0.04 wt.% $Pd–Ag/Al_2O_3$ (treated)	4.98

N_2O-treated catalyst was slightly higher than that of the untreated one. This reflects that two silver atoms may move closely to one oxygen atom to form Ag_2O. This phenomenon can expose the active palladium sites which is normally located under the surface of metal cluster as modeled in Fig. 2.

Table 3 shows the metal active sites of catalysts measured by CO adsorption. It has been found that the Ag-promoted Pd catalyst exhibited less amount of active sites than that of the unpromoted one. This may be due to the alloy formation between both metals. The addition of N_2O to the silver-promoted catalyst was found to enhance the amount of active sites which also supported the proposed model as described above. The highest amount of active sites was achieved with the injection of 0.1 cm^3 of N_2O.

Table 3
The metal active sites of catalysts measured by CO adsorption

Catalyst	Metal active sites (sites/g of catalyst)
0.04 wt.% Pd/Al_2O_3	3.30×10^{17}
0.04 wt.% $Pd–Ag/Al_2O_3$	2.52×10^{17}
0.04 wt.% $Pd–Ag/Al_2O_3$ (0.02 cm^3 of N_2O)	3.14×10^{17}
0.04 wt.% $Pd–Ag/Al_2O_3$ (0.035 cm^3 of N_2O)	3.22×10^{17}
0.04 wt.% $Pd–Ag/Al_2O_3$ (0.05 cm^3 of N_2O)	3.70×10^{17}
0.04 wt.% $Pd–Ag/Al_2O_3$ (0.10 cm^3 of N_2O)	4.04×10^{17}
0.04 wt.% $Pd–Ag/Al_2O_3$ (0.15 cm^3 of N_2O)	3.37×10^{17}
0.04 wt.% $Pd–Ag/Al_2O_3$ (0.33 cm^3 of N_2O)	3.18×10^{17}

4. Conclusion

It might be concluded that N_2O treatment could improve the catalytic performance of the silver-promoted palladium catalyst by enhancing the accessible sites of active Pd responsible for ethylene production from acetylene, and meanwhile decreasing the sites involving the direct ethane formation from acetylene. Furthermore, the N_2O-treated catalyst has the same stability as the untreated one during the aging period.

Acknowledgements

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