Catalysis Letters Vol. 86, Nos. 1–3, March 2003 (© 2003)

Acetylene hydrogenation on Au-based catalysts

T.V. Choudhary [a,*], C. Sivadinarayana [a], A.K. Datye [b], D. Kumar [a], and D.W. Goodman [a,†]

[a] *Department of Chemistry, Texas A&M University, College Station, TX 77842, USA*
[b] *Chemical Engineering Department, University of New Mexico, Albuquerque, New Mexico, USA*

Received 23 September 2002; accepted 12 November 2002

Hydrogenation of acetylene has been investigated on Au/TiO_2, Pd/TiO_2 and Au–Pd/TiO_2 catalysts at high acetylene conversion levels. The Au/TiO_2 catalyst (avg. particle size: 4.6 nm) synthesized by the temperature-programmed reduction–oxidation of an Au–phosphine complex on TiO_2 showed a remarkably high selectivity to ethylene formation even at 100% acetylene conversion. Au/TiO_2 prepared by the conventional incipient wet impregnation method (avg. particle size: 30 nm), on the other hand, showed negligible activity for acetylene hydrogenation. Although the Au catalysts showed a high selectivity for ethylene, the acetylene conversion activity and catalyst stability were inferior to the Pd-based catalysts. Au–Pd catalysts prepared by the redox method showed high acetylene conversions as well as high selectivity for ethylene. Interestingly Au–Pd catalysts prepared by depositing Pd via the incipient wetness method on Au/TiO_2 showed very poor selectivity (comparable to mono-metallic Pd catalysts) for ethylene. High-resolution transmission electron microscopy (TEM) studies coupled with energy dispersive X-ray spectroscopy (EDS) showed that while the redox method produced bimetallic Au–Pd catalysts, the latter method produced individual Pd and Au particles on the support.

KEY WORDS: acetylene hydrogenation; Au catalysts; gold.

1. Introduction

Ethylene obtained from thermal cracking and steam cracking contains small quantities of acetylene (<2%) which acts as a poison for ethylene polymerization catalysts. Typically Pd-based catalysts are employed to eliminate these trace amounts of acetylene from ethylene streams. High selectivity for ethylene and long-term catalyst stability is particularly desired for the selective acetylene hydrogenation process.

The selective hydrogenation of trace acetylene has been extensively investigated over Pd and promoted Pd catalysts. Due to the extremely low tolerance for acetylene of polymerization catalysts, extremely high conversions of acetylene are required (concentration of acetylene in the effluent stream should be lower than 10 ppm). However, since hydrogenation of acetylene is a series reaction (acetylene → ethylene → ethane), the selectivity for ethylene decreases drastically with increasing acetylene conversion. Although unpromoted Pd catalysts have high activity for trace acetylene elimination they suffer from low ethylene selectivity at high acetylene conversion levels. Addition of promoters such as Ag, Co, Cu, Cr, alkali metals, lead acetate and metal oxides is known to improve the performance of Pd catalysts [1–5].

Although most of the selective acetylene hydrogenation studies to date have involved Pd-based systems, other catalysts have also been considered [6–8]. A recent acetylene hydrogenation study has shown that well-dispersed Au catalysts show extremely high selectivity for ethylene formation [6]. These studies were carried out in a batch reactor (closed gas circulating system); moreover they provided no information about catalyst stability. In this paper, we have investigated the acetylene hydrogenation reaction on Au/TiO_2 catalysts (average particle size: 4.6 nm) at high conversions in a continuous flow system. Au catalysts with larger particles (average particle size: 30 nm) have also been investigated for comparison. The Au catalysts have been characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and the low-temperature CO oxidation reaction.

We have also investigated the promotion of Au catalysts with Pd and compared the activity/selectivity of these catalysts with the mono-metallic Au and Pd catalysts. The acetylene hydrogenation reaction has been studied on Au–Pd catalysts prepared by two different methods: (a) a redox method [9,10], and (b) deposition of Pd by the incipient wetness method on Au/TiO_2 catalysts which were prepared by the deposition–precipitation method. High-resolution TEM coupled with energy dispersive X-ray spectroscopy (EDS) was employed to study the nature of the Pd–Au interaction in the two catalysts prepared by the different methods.

2. Experimental

2.1. Catalyst synthesis

TiO_2 (Degussa P-25; surface area 35–65 m^2/g), which was used as the support for all these catalysts, was

---

[*] Present address: Phillips Petroleum Company, Bartlesville, OK 74004, USA.
[†] To whom correspondence should be addressed.
E-mail: goodman@mail.chem.tamu.edu

1011-372X/03/0300-0001/0

calcined at 500 °C for 4 h prior to the synthesis procedure. The Au(I)/TiO_2 catalyst was prepared by grafting an $[Au_6(PPu_3)_6](BF_4)_2$ complex onto TiO_2. A CH_2Cl_2 solution of the Au complex was used to wet the TiO_2 support. After drying at room temperature the catalyst was further treated by heating in 1:2 H_2 + He mix at 500 °C for 0.5 h and calcining in 1:2 air + He mixture for 0.5 h at 400 °C. Further details of the synthesis are provided elsewhere [11]. Au(II)/TiO_2 was prepared by impregnating TiO_2 with an aqueous solution of chloroauric acid. Following this, the catalyst was dried at 80 °C (overnight) and calcined at 400 °C for 4 h.

The following procedure was employed for the synthesis of the Au–Pd(I)/TiO_2 catalyst. The support TiO_2 particles were suspended in an aqueous solution of chloroacuric acid (pH 7.5; adjusted with 1 M NaOH solution) at 80 °C for 1 h. After washing and drying the suspension was calcined at 400 °C for 4 h. This procedure (deposition–precipitation) was employed to produce highly dispersed Au particles. An aqueous solution of Pd nitrate was then used to deposit Pd. The material so obtained was dried overnight and then calcined for 3 h at 400 °C and reduced in H_2/He for 1 h at 350 °C.

An aqueous solution of Pd nitrate was employed to impregnate TiO_2 for the synthesis of the Pd_{imp}/TiO_2. After overnight drying at 80 °C, the catalyst was calcined for 3 h at 400 °C and reduced in H_2/He for 1 h at 350 °C. The Au–Pd(II)/TiO_2 catalyst was prepared by the redox method [9]. A portion of the Pd_{imp}/TiO_2 (after the reduction treatment) was suspended in deionized water, and the solution continuously stirred with bubbling Ar and H_2. After 0.5 h, the H_2 flow was stopped. Following this, an aqueous solution of chloroauric acid was slowly introduced. After 1 h, the resulting solid was separated by filtration, washed and dried overnight at 80 °C. The material was then calcined at 400 °C for 3 h and reduced in a H_2/He mixture at 350 °C for 1 h. Unless specified otherwise the catalysts were calcined using a flow of air and a temperature ramp rate of 3 °C/min.

2.2. Catalyst characterization

2.2.1. TEM

TEM studies were carried out using a high-resolution JEOL 2010 microscope (operated at 200 keV) at the University of New Mexico. Samples were supported on copper grids with holed carbon films by dipping the grid in the sample powder and shaking the excess. Several bright-field TEM images of different portions of the sample were obtained at magnifications up to 400 000. At least 100 particles were employed to determine the average particle size.

2.2.2. XPS and X-ray diffraction (XRD)

XPS was performed using an ion-pumped (300 L/s) Perkin-Elmer PHI 560 system using a PHI 25-270AR double pass cylindrical mirror analyzer. Samples were mounted onto a 1.0 cm × 1.0 cm × 1.0 cm support using double-sided tape (Scotch 3M) attached to a probe and introduced into the UHV via a turbo-pumped antechamber. Detailed information regarding the XPS apparatus is published elsewhere [12]. The XRD measurements were performed using CuKα radiation and a Phillips PW 1820 goniometer with a Bragg–Brentano geometry.

2.2.3. Determination of metal content

The samples were digested in aqueous HF solutions and analyzed using a SpectraSpan VI DCP (Applied Research Laboratories) operating with Adam VI software. Table 1 summarizes the metal content for the different catalysts prepared.

2.2.4. CO oxidation

The CO oxidation reaction was used to characterize the Au(I)/TiO_2 and Au(II)/TiO_2 catalysts. The CO oxidation activity was measured in a conventional fixed-bed reactor in a quartz reactor at CO and O_2 partial pressures of 27.5 torr and temperatures ranging from ambient to 150 °C. The gas analysis system consisted of a Varian 3700 gas chromatograph equipped with a thermal conductivity detector and carbosphere column for gas separation. CO (research purity; Matheson), O_2 (UHP; Matheson) and He (UHP; Matheson) were employed for the study.

2.3. Acetylene hydrogenation

The acetylene hydrogenation experiments were carried out in a conventional flow reactor system consisting of a

Table 1
Catalyst composition

Catalyst	Method of preparation	Metal content (wt%)	
		Pd	Au
Au(I)/TiO_2	Grafting	–	0.95
Au(II)/TiO_2	Impregnation		0.92
Pd_{imp}/TiO_2	Impregnation	0.53	–
Au–Pd(I)/TiO_2	Impregnation/deposition–precipitation	0.48	0.98
Au–Pd(II)/TiO_2	Redox	0.53	1.15

quartz reactor, custom-built furnace and an omega temperature controller which could be employed to ramp the temperature at the desired heating rate. While 20 mg was used for the reaction for Pd-containing catalysts, 150 mg was used in case of Au(I)/TiO_2 and Au(II)/TiO_2 catalysts. The on-line gas analysis system consisted of a Carle gas chromatograph equipped with a flame ionization detector. While only the C_2 gases were detected regularly, occasionally the entire hydrocarbon range was detected using an off-line Varian gas chromatograph equipped with a capillary column. High-purity gases, 5% C_2H_2 in He (Matheson; Certified Mixture), H_2 (UHP; Matheson) and He (UHP; Matheson), were employed for the study.

The selectivity for C_2H_4 was defined as: % selectivity (C_2H_4) = 100 × [C_2H_4 (product)/C_2H_2 (feed) − C_2H_2 (product)].

3. Results and discussion

Although historically Au has been considered to be ineffective as a catalyst, recent studies have shown that highly dispersed Au particles (avg. particle size <5 nm) can catalyze a variety of reactions [13]. In fact supported nano-Au particles are now considered to be the most active catalysts for the low-temperature CO oxidation reaction. In this study the acetylene hydrogenation reaction has been investigated in a continuous flow reactor over Au/TiO_2 catalysts with high and low Au dispersions. Figure 1(a) shows a TEM image of the Au(I)/TiO_2 catalyst, which was prepared by the reduction–oxidation treatment of a $[Au_6(PPh_3)_6](BF_4)_2$ complex on TiO_2. The Au particles exhibited an average particle size of 4.7 nm. Although the particle size distribution ranged from 2 to 8 nm, the majority of the Au particles fell within the range 3–6 nm (figure 1(b)). XPS studies showed a shift from higher binding energy (84.7 eV) for as-synthesized Au(I)/TiO_2 catalysts to lower binding energy (83.7 eV) for the Au $4f_{7/2}$ level after the high-temperature reduction–oxidation treatment (>673 K). This is in good agreement with the transformation of the Au–phosphine complex to metallic Au particles as reported in the literature. It is noteworthy that pre-treatment conditions had a significant effect on the particle size distribution of these Au catalysts prepared from the Au–phosphine complex. A detailed TEM and XPS study involving the effect of pre-treatment conditions is reported elsewhere [11].

The Au(II)/TiO_2 catalysts prepared by impregnation of TiO_2 with an aqueous chloroauric solution showed poor dispersion; an average Au particle size of 30 nm was observed in this case. Unlike the Au(I)/TiO_2 catalysts, a reduction–oxidation treatment does not significantly affect the particle size distribution of the Au(II)/TiO_2 catalysts [14].

The CO oxidation reaction was used to further characterize the Au/TiO_2 catalysts (figure 2). At room temperature, the CO oxidation activity of the well-dispersed Au(I)/TiO_2 catalyst was an order of magnitude higher than that of the Au(II)/TiO_2 catalyst. While a 100% CO conversion was observed for the Au(I)/TiO_2 catalyst at 120 °C, the CO conversion was less than 20% for the Au(II)/TiO_2 catalyst at the same temperature. It is noteworthy that the CO oxidation activity for the Au(I)/TiO_2 catalyst was comparable to other highly dispersed Au catalysts prepared by deposition–precipitation and chemical vapor deposition methods [11,15].

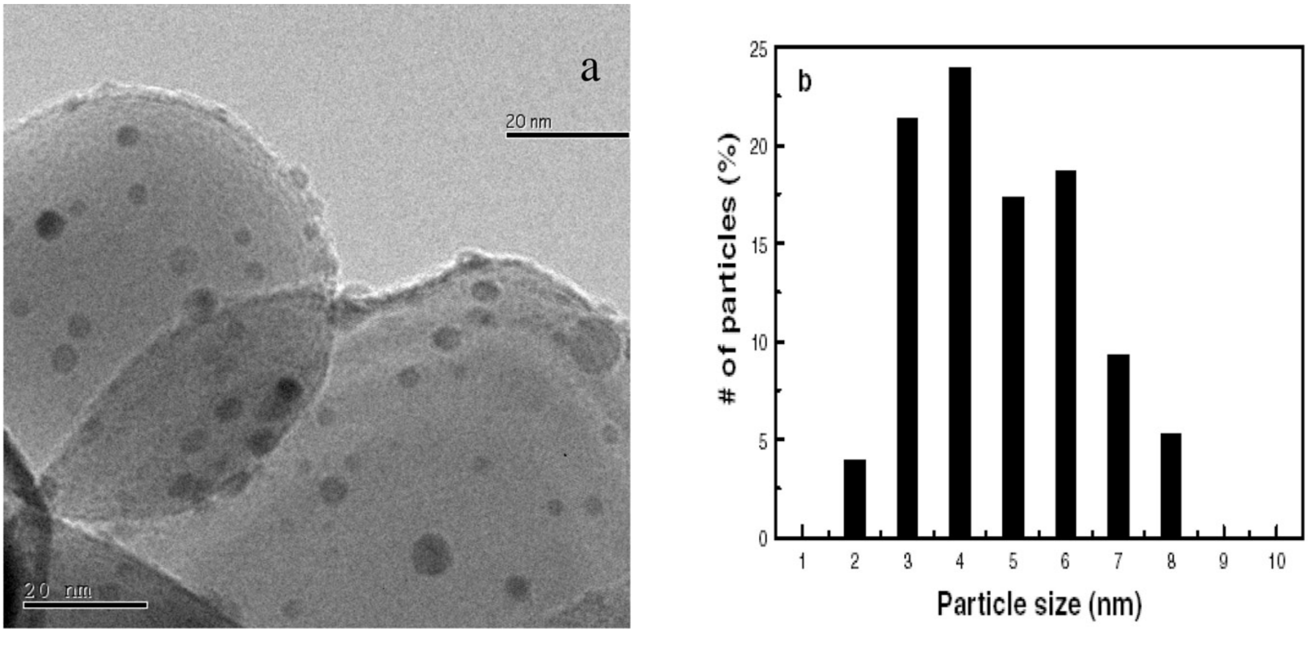


Figure 1. (a) Representative TEM image of the Au(I)/TiO_2 catalyst. (b) Particle size distribution.

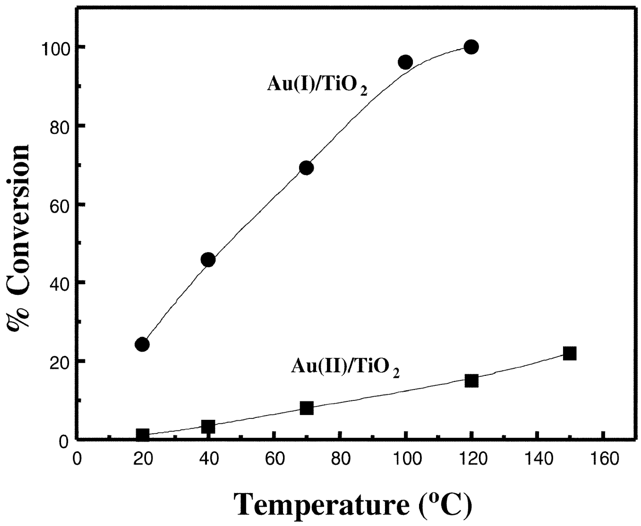


Figure 2. Comparison of the CO oxidation activity for the well-dispersed Au(I)/TiO$_2$ and poorly dispersed Au(II)/TiO$_2$ catalysts.

Figure 3 shows the time on stream C_2H_2 hydrogenation activity/selectivity for the Au(I)/TiO$_2$ catalyst at 180 °C (1% C_2H_2; $H_2/C_2H_2 = 4$). The catalyst showed a high initial activity with 100% C_2H_2 conversion. Most importantly, the selectivity for ethylene was found to be extremely high (>90%) even at complete conversion of acetylene. In good agreement, Tamaru and co-workers [6] observed essentially no ethane formation over a 10% Au/Al_2O_3 catalyst in the temperature range between 40 and 250 °C in a closed gas circulating system (batch reactor).

However, the time on stream study indicated that the Au catalyst was not stable and continuously deactivated with time. Over a period of three hours the acetylene conversion decreased from 100 to 82%. Interestingly time on stream CO oxidation studies on the same catalyst at 80 °C showed stable activity for several hours [11]. The deactivation in the case of the acetylene hydrogenation reaction may be attributed to poisoning by carbon or sintering of the Au particles. The catalyst was found to regain its original activity following regeneration using a reduction (500 °C) and oxidation (400 °C) treatment, suggesting that the deactivation mechanism involved carbon poisoning. The Au(II)/TiO$_2$ catalyst showed extremely poor activity for acetylene hydrogenation at 180 °C; the C_2H_2 conversion was less than 5%. This is in excellent agreement with the CO oxidation activity trend observed for the two Au catalysts with different dispersions. This clearly suggests that, similar to the CO oxidation reaction, the Au catalyst needs to be in a highly dispersed form to be active for the acetylene hydrogenation reaction.

Hydrogenation of acetylene involves the following series reactions: $C_2H_2 \rightarrow C_2H_4 \rightarrow C_2H_6$. Subsequent conversion of reaction intermediate ethylene to ethane is profoundly influenced by its interaction with the catalyst surface. Since acetylene preferentially adsorbs on the catalyst surface with respect to ethylene, the ethylene selectivity is high at low acetylene conversion, and drastically decreased under conditions approaching complete acetylene conversion. In order to differentiate clearly between the ethylene selectivity performance for the various catalysts in this work, studies were undertaken at high conversions of acetylene. Figure 4(a) shows the ethylene selectivity for the acetylene hydrogenation reaction for different Pd-based catalysts at 70 °C (1% C_2H_2; $H_2/C_2H_2 = 2.5$). Each of the catalysts showed 100% acetylene conversion (not shown) under the reaction conditions employed. The selectivity for ethylene formation was not significantly different for the Pd$_{imp}$/TiO$_2$ and the Au–Pd(I)/TiO$_2$ catalysts; after a period of 4 h the ethylene selectivity for the two catalysts was 11

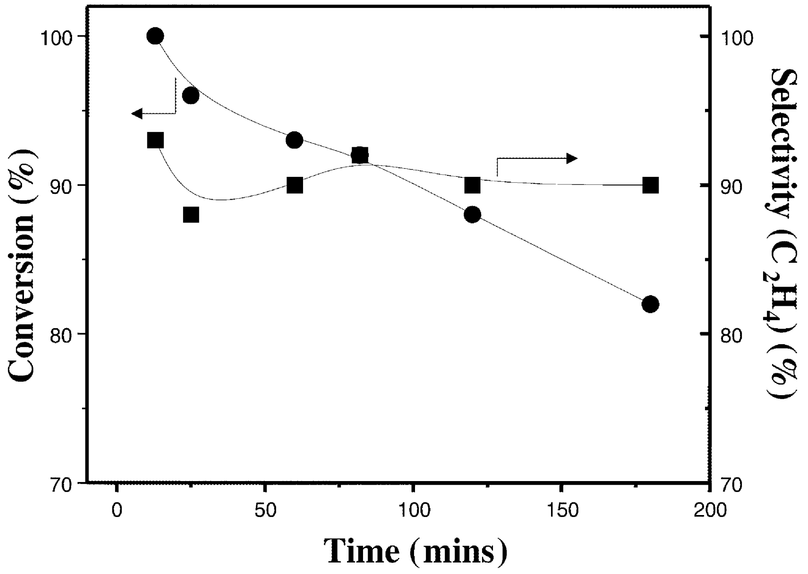


Figure 3. Time on stream acetylene hydrogenation activity for the Au(I)/TiO$_2$ catalyst at 180 °C. GHSV = 12 000 cm^3/g/h (1% C_2H_2; $H_2/C_2H_2 = 4$).

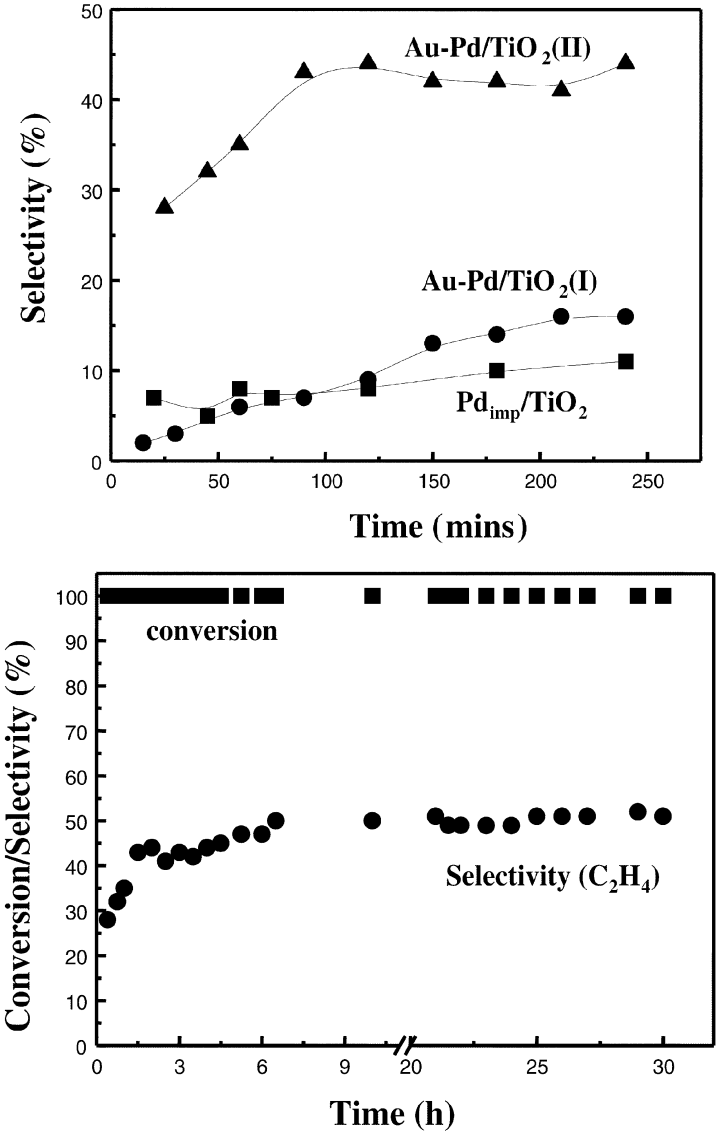


Figure 4. (a) Time on stream ethylene selectivity for the different Pd-based catalysts at 70 °C. GHSV = 90 000 cm^3/g/h (1% C_2H_2; $H_2/C_2H_2 = 2.5$). (b) Time on stream performance for the Au–Pd(II)/TiO_2 catalyst for the acetylene hydrogenation reaction at 70 °C, GHSV = 90 000 cm^3/g/h (1% C_2H_2; $H_2/C_2H_2 = 2.5$).

and 15% respectively. However, the ethylene selectivity for the Au–Pd(II)/TiO_2 catalyst was far superior. After 1.5 h into the acetylene hydrogenation reaction the selectivity for ethylene stabilized at about 45%. Figure 4(b) shows the performance of the Au–Pd(II)/TiO_2 catalyst for the acetylene hydrogenation reaction for a period of 30 h. The conversion remained at 100% throughout the reaction period indicating no significant deactivation. The ethylene selectivity increased with time initially and finally stabilized at about 51% after a period of 6 h.

Table 2 compares the performance of the various catalysts after 2 h into the acetylene hydrogenation time on stream reaction. The Au(I)/TiO_2 catalyst exhibited superior ethylene selectivity for the acetylene hydrogenation reaction. C_{2+} formation was also significantly lower for the Au catalyst. However, it should be noted that the Au catalyst exhibited poor stability with respect to the Pd-based catalysts. Moreover the acetylene hydrogenation activity was also significantly lower for the Au(I)/TiO_2 catalyst (required higher temperature, higher H_2/C_2H_2 ratio and higher

Table 2

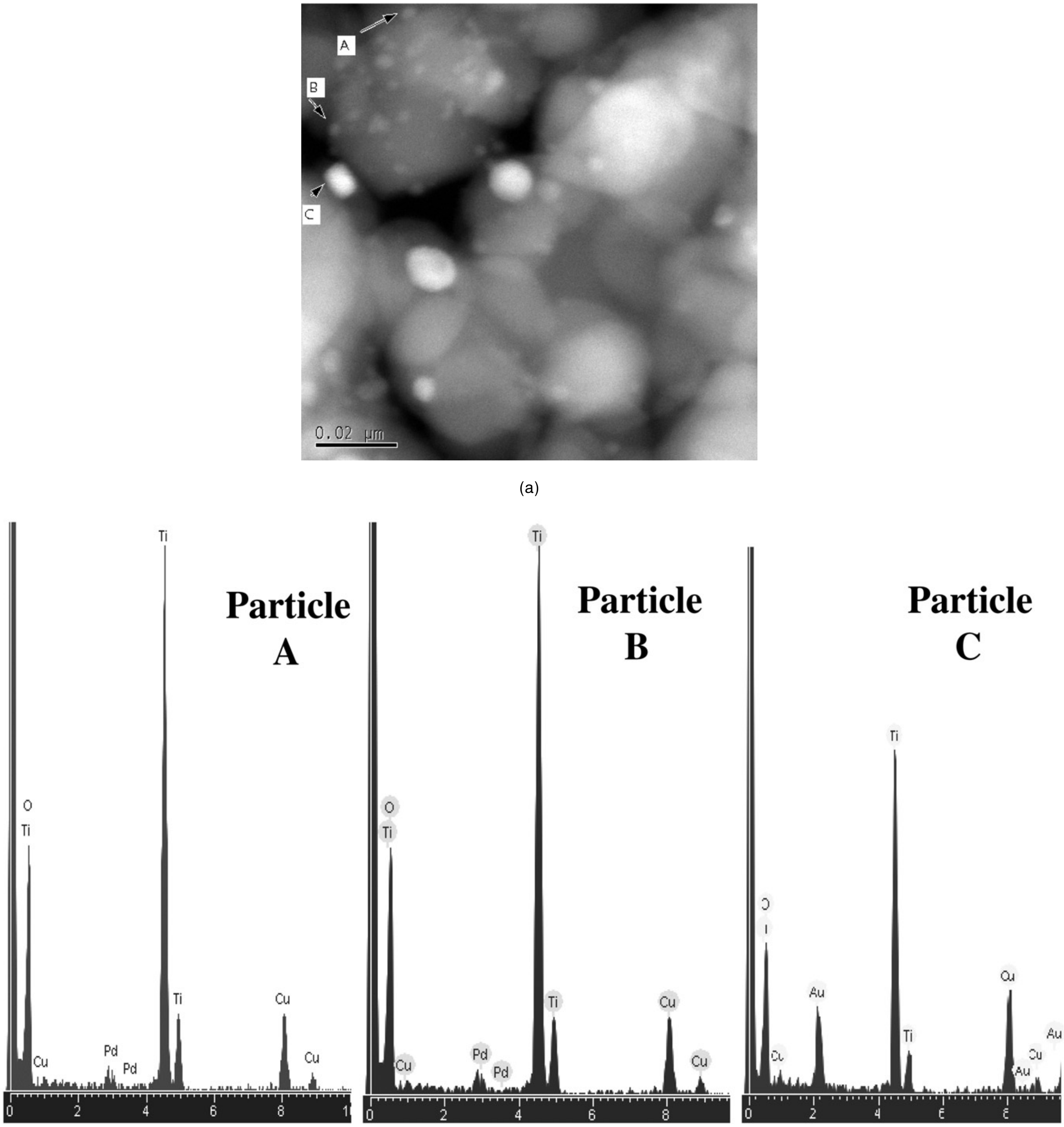
Acetylene hydrogenation comparison for the catalysts after 2 h time on stream (1% C_2H_2). Unless specified GHSV = 90 000 cm^3/g/h and $H_2/C_2H_2 = 2.5$

Catalyst	Temperature (°C)	Conversion (%)	C_2H_4 selectivity (%)
Au(I)/TiO_2 [a]	180	88	90
Pd_{imp}/TiO_2	70	100	8
Au–Pd(I)/TiO_2	70	100	9
Au–Pd(II)/TiO_2	70	100	45

[a] GHSV = 12 000 cm^3/g/h and $H_2/C_2H_2 = 4$.

contact time). Promotion of the Au catalyst with Pd yielded interesting results. While the ethylene selectivity was 9% for the Au–Pd(I)/TiO_2 catalyst, it was 45% for the Au–Pd(II)/TiO_2 catalyst. It is thus apparent that although the Pd impregnation method resulted in an ineffective catalyst (similar to mono-metallic Pd catalyst), the redox method produced a significantly superior catalyst showing high ethylene selectivity at complete acetylene conversion. A recent pulse reactor study [16] also indicated a higher ethylene selectivity on Pd–Au catalysts (redox method), although significantly less than in this study. This difference may be attributed to the fact that these were pulse reactor studies and were carried out at extremely low acetylene conversion levels. Moreover the Pd–Au catalyst used in this study has a significantly higher Au/Pd ratio.

In order to understand the drastically different catalytic behavior of the Au–Pd(I)/TiO_2 and Au–Pd(II)/TiO_2



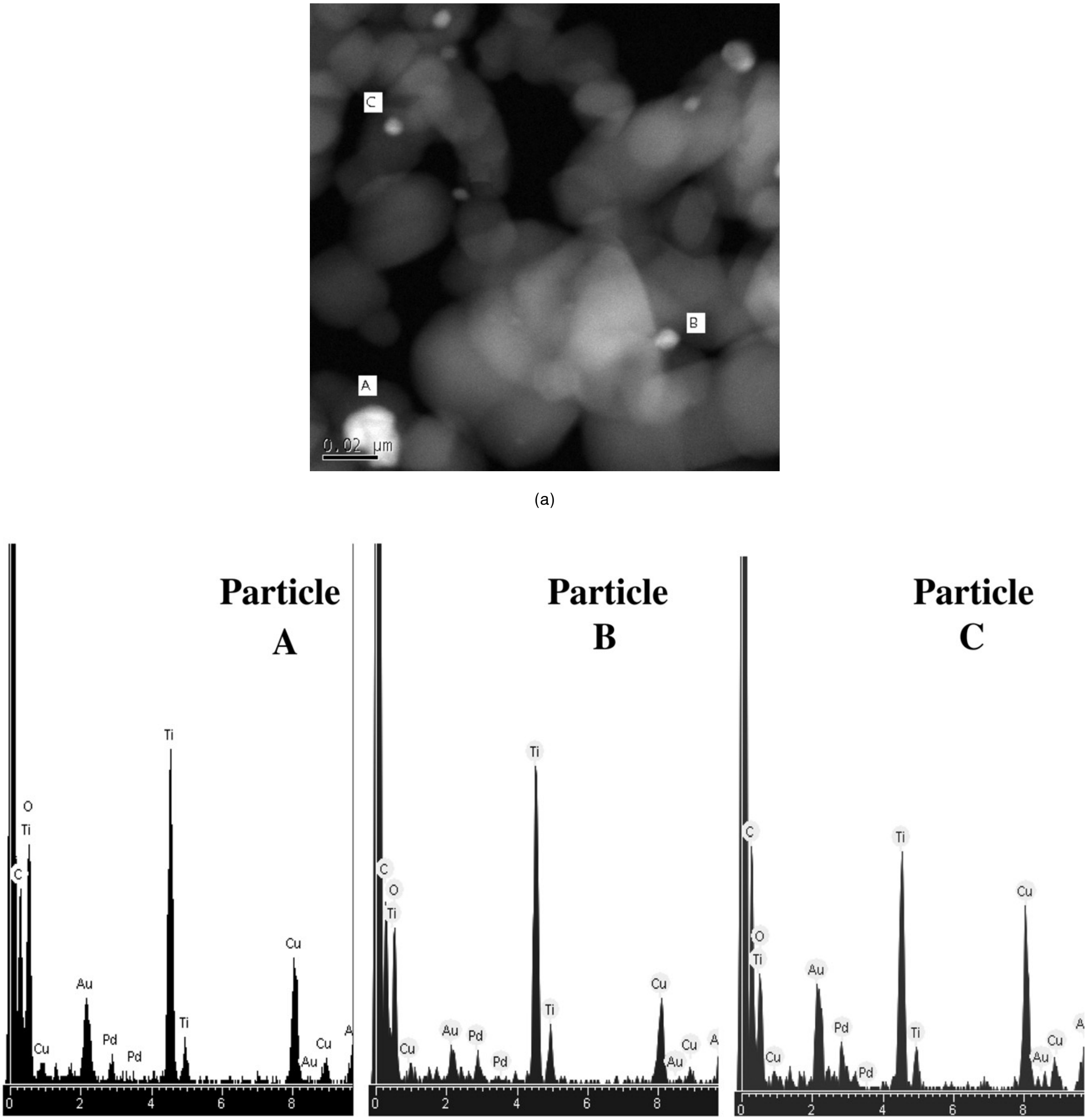
(a)

(b)

Figure 5. (a) TEM image of the Au–Pd(I)/TiO_2 catalyst. (b) The corresponding EDS patterns.

catalysts, initially XRD was considered. However, the interference of support TiO_2 diffraction peaks in the region of interest precluded the effective use of this technique. To circumvent this problem, TEM coupled with EDS was employed to understand the nature of the Pd–Au interaction for the two catalysts. Figure 5(a) shows the TEM image of the Au–Pd(I)/TiO_2 catalyst; the corresponding EDS patterns for some representative particles are shown in figure 5(b) (particles A, B, C). The results clearly show that the Pd impregnation procedure on Au/TiO_2 results in a catalyst with individual Pd and Au particles on the support. The TEM and EDS results for the Au–Pd(II)/TiO_2 catalyst are shown in figure 6 (particles A, B, C). EDS shows the presence of both Pd and Au in the particles, thus indicating a close interaction between the two. It is noteworthy that the composition of the Au–Pd catalyst from EDS (significantly richer in Au content) compared well with the metal composition obtained from AAS.

The combined TEM and EDS investigation on the Au–Pd(I)/TiO_2 and Au–Pd(II)/TiO_2 catalysts can be effectively used to explain the difference in catalytic



(a)

(b)

Figure 6. (a) TEM image of the Au–Pd(II)/TiO_2 catalyst. (b) The corresponding EDS patterns.

selectivity for the acetylene hydrogenation reaction for the two catalysts of similar Au/Pd content. For the Au–Pd(I)/TiO_2 catalyst, there is no interaction between Pd and Au, therefore the catalyst behaves essentially as a mono-metallic Pd catalyst. This follows from the fact that Au has no significant acetylene hydrogenation activity at 70 °C. On the other hand, the Au–Pd(II)/TiO_2 catalyst prepared by the redox method is clearly bimetallic, which is in good agreement with previous characterization studies (XRD and temperature-programmed hydride decomposition) of Pd–Au/SiO_2 catalysts prepared by the redox method [10].

One of the main pathways for ethane synthesis (decrease in ethylene selectivity) during acetylene formation is via the hydrogenation of surface intermediate species such as ethylidene and ethylidyne [17]. The formation of these intermediate species requires the presence of multiple Pd sites. For the Au–Pd(II)/TiO_2 catalyst, the presence of excess Au should dramatically decrease the multiple Pd sites and thus eliminate a major pathway for ethane formation. Since the Au(I)/TiO_2 catalyst showed an extremely high selectivity for ethylene formation, it is speculated that the presence of Au in Au–Pd(II)/TiO_2 also modifies the adsorption properties of acetylene and ethylene, leading to higher ethylene selectivity. Model studies to further explore the nature of the interaction between Pd and Au and their chemistry with acetylene/ethylene/ethane are the subject of ongoing studies.

4. Conclusions

The performance of Au-based catalysts for the acetylene hydrogenation reaction has been evaluated in comparison to single-component Pd catalysts. The highly dispersed Au/TiO_2 catalyst prepared by the reduction–oxidation of an Au–phosphine complex on TiO_2 showed extremely high ethylene selectivity even at complete acetylene conversion. However, it suffered from inferior activity and stability as compared to a mono-metallic Pd catalyst. The Pd-promoted Au catalyst prepared by the redox method showed significantly higher ethylene selectivity at 100% acetylene conversion as compared to a mono-metallic Pd catalyst under similar reaction conditions. Moreover the Au–Pd catalyst also showed excellent stability over several hours. Characterization studies revealed that a close interaction of Au and Pd was essential for superior ethylene selectivity as a catalyst composed of individual Au and Pd particles exhibited similar performance to a mono-metallic Pd catalyst.

Acknowledgment

We acknowledge with pleasure the support of this work by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, and the Robert A. Welch Foundation.

References

[1] Y.H. Park and G.L. Price, Ind. Eng. Chem. Res. 31 (1992) 469.
[2] V. Ponec and G.C. Bond, Stud. Surf. Sci. Catal. 95 (1995) 491.
[3] J. Phillips, A. Auroux, G. Bergeret, A. Massardier and J. Renoupez, J. Phys. Chem. 97 (1993) 3565.
[4] J.H. Kang, E.W. Shin, W.J. Kim, J.D. Park and S.H. Moon, Catal. Today 63 (2000) 183.
[5] Y. Jin, A.K. Datye, E. Rightor, R. Gulloty, W. Waterman, M. Smith, M. Holbrook, J. Maj and J. Blackson, J. Catal. 203 (2001) 2001.
[6] J. Jia, K. Haraki, J.N. Kondo, K. Domen and K. Tamaru, J. Phys. Chem. B 104 (2000) 11153.
[7] A. Onda, T. Komatsu and T. Yashima, Phys. Chem. Chem. Phys. 2 (2000) 2999.
[8] V. Rives, F.M. Labajos, R. Trujillano, E. Romeo, C. Royo and A. Monzon, Appl. Clay Sci. 13 (1998) 363.
[9] J. Barbier, P. Marecot, G. Del Angel, P. Bosch, J.P. Boitiaux, B. Didillon, J.M. Dominguez, I. Schifter and G. Espinoza, Appl. Catal. A 116 (1994) 179.
[10] M. Bonarowska, J. Pielaszek, W. Juszczyk and Z. Karpinski, J. Catal. 195 (2000) 304.
[11] T.V. Choudhary, C. Sivadinarayana, C.C. Chusuei, A.K. Datye, J.P. Fackler, Jr. and D.W. Goodman, J. Catal. 207 (2002) 247.
[12] T.V. Choudhary, C. Sivadinarayana, C. Chusuei, A. Klinghoffer and D.W. Goodman, J. Catal. 199 (2001) 9.
[13] G.C. Bond and D.T. Thompson, Catal. Rev. Sci. Eng. 41 (1999) 319.
[14] S.D. Lin, M. Bollinger and M.A. Vannice, Catal. Lett. 17 (1993) 245.
[15] T.V. Choudhary and D.W. Goodman, Top. Catal. 21 (2002) 25.
[16] A. Sárkány, A. Horváth and A. Beck, Appl. Catal. A 229 (2002) 117.
[17] S. Leviness, V. Nair, A.H. Weiss, Z. Schay and L. Guczi, J. Mol. Catal. 25 (1984) 131.