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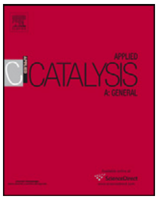

Some features of acetylene hydrogenation on Au-iron oxide catalyst

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ABSTRACT

Hydrogenation of acetylene has been investigated on Au-iron oxide catalysts containing 4.5, 3.0, 5.6 wt% Au prepared by deposition–precipitation (DP) with urea, adsorption of Au sol (SA) and by co-precipitation (CP) of $HAuCl_4$ and $Fe(NO_3)_3$, respectively. The latter method produced Au particles supported on 2-line ferrihydrite ($Fe_5HO_8{\cdot}4H_2O$). Au/iron oxide catalyst precursors (Au/α-Fe_2O_3 and Au/2-line ferrihydrite) were characterized by BET, TGA, TPR and XRD, and the Au particle size by TEM measurements. The TPR measurements confirm the ease of transformation of 2-line ferrihydrite to magnetite (Fe_3O_4) and that the formation of magnetite from α-Fe_2O_3 depends strongly on the size of the gold and the supporting oxide particles. Particle size effect of gold has been investigated in semi-hydrogenation of acetylene. Temperature of hydrogen treatment has been observed to play a crucial role in the activity and ethylene selectivity. Au/FeO_x samples hydrogen treated at 353–473 K prior to introduction of the reactants (H_2:C_2H_2 = 140, 0.11% C_2H_2) show very limited over-hydrogenation (ethane formation is less than ≈1%) and 2–4% selectivity of oligomer (C4+) formation at 353–473 K. Hydrogen treatment of the samples at $T > 573$ K but lower than the wüstite (FeO) stability point (≈843 K) resulted in partial reduction of Fe_3O_4 and formation of Fe^0. The shift of Au(1 1 1) XRD line to higher 2Θ provided evidence for the incorporation of Fe^0 into the Au particles. Modification of the Au/Fe_2O_3 perimeter and appearance of Fe^0 co-catalyst and Fe–Au ensembles on the surface increased the hydrogenation activity but decreased the selectivity of ethylene formation.

1. Introduction

Recently considerable attention focused on application of gold nanoparticles in catalytic reactions such as CO oxidation, preferential CO oxidation in hydrogen (PROX), water gas shift reaction, selective partial oxidation or hydrogenation [1–4]. In nanosized form gold has been reported to be active in hydrogenation of acrolein [5], 1,3-butadiene [1] or α,β-unsaturated ketones [6,7]. In semi-hydrogenation of acetylene or propyne Au shows rather low activity in comparison with transition metals [8–13]. Removal of alkyne impurities such as acetylene or propyne is an industrially important reaction to upgrade alkene streams with the intention to produce polymerisation grade olefin [14–16]. Conventionally ethylene is purified over Pd based catalyst to remove acetylene contaminant from about 4000 ppm to 5 ppm in slight excess of hydrogen [14–16]. To improve the ethylene selectivity Pd is frequently promoted with Ag, Au or Cu [15,17–20]. However, in large excess of hydrogen ("front-end" composition in the separation train) the Pd catalysts are not selective enough in semi-hydrogenation of alkynes [15,17–20]. In order to avoid over-hydrogenation CO moderation of Pd is almost unavoidable. CO is considered to compete with ethylene and decreases the hydrogen availability on the Pd sites [14–16]. The low hydrogen coverage on Au has focused some attention on its hydrogenation activity and selectivity [8–13].

On both Au/Al_2O_3 [8] and Au/CeO_2 [12] high selectivity of acetylene hydrogenation was reported in the 323–523 K temperature range. In contrast, only 90% ethylene selectivity and over-hydrogenation (ethane formation) was observed on Au/TiO_2 [9] at 453 K. In propyne hydrogenation at 473–573 K over 2.6 wt% Au/CeO_2 catalyst Segura et al. [10] found 80–95% propene selectivity. Lennon and co-worker [11] in pulse adsorption–hydrogenation studies confirmed retention of hydrocarbons on the surface. Depending on the experimental conditions the authors observed [11] selective or non-selective propene formation from adsorbed propyne over Au/TiO_2 and Au/Fe_2O_3. Investigations on Au/SiO_2 [13] prepared by fixation of Au sol of 3.7 nm to SiO_2 confirmed the high ethylene selectivity even in large excess of hydrogen. Smaller amount of deposit was observed on Au/SiO_2 than on Au/TiO_2 catalyst [13].

Inspection of the reports above allows one to conclude that high alkene selectivity can be achieved on gold particles [8,12,13], but at low H_2:C_2H_2 ratios the Au catalysts suffer fast deactivation

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[8,9,12,13]. The rapid poisoning can be explained by the ease of deposit formation due to the low hydrogen coverage on Au sites [21–24]. Over-hydrogenation [9,10] or less selective behaviour may be the consequence of high reaction temperature or the modification of the Au-support interface. In this paper we report a study on acetylene hydrogenation over Au-iron oxide catalysts prepared by deposition–precipitation (DP), Au sol adsorption (SA) and co-precipitation (CP) methods. Co-precipitation of Fe(III) and Au(III) solutions is a suitable method to produce Au particles of high dispersion [6,7,25]. As acetylene hydrogenation on Au/FeO_x catalysts was not reported yet we decided to check the particle size sensitivity of the product formation. FeO_x is one of the reducible oxides therefore it was our intention to investigate the effect of hydrogen treatment on catalytic activity and selectivity. The Au–FeO_x support interface and the support itself should change upon reduction treatment. Only trace amount of acetylene was hydrogenated in large excess of hydrogen (H_2:C_2H_2 = 140, 0.11% C_2H_2) to facilitate hydrogen availability on Au sites and suppress formation of various types of carbonaceous deposit. The actual working state of Au/FeO_x with respect to deposit formation was investigated by temperature-programmed oxidation (TPO).

2. Experimental

2.1. Catalyst preparation

DP, SA and CP techniques were applied to prepare Au/iron oxide catalysts. Au/α-Fe_2O_3 (further on AuS1) was prepared by deposition of gold on commercial α-Fe_2O_3 (further on S1, produced by Reanal, Hungary) of low surface area. The surface area of the oxide support (S1) is 9.2 $m^2 g^{-1}$ (see Table 1). Au was deposited on the support from $HAuCl_4$ at 358 K by slow hydrolysis of urea [26]: 1 g of Fe_2O_3 was mixed with solution of $HAuCl_4$ and urea (0.66 M) and heated to 358 K for 3 h. The sample was washed, dried and finally calcined at 673 K in 1% O_2 to remove impurities originating from urea.

AuS2 was prepared the following way: first Au sol was synthesised from $HAuCl_4$ in the presence of tannin and sodium citrate [27]. The average zeta potential of the sol is −28 mV at pH ≈ 5–6 [28]. Next, the support was prepared at pH 7.7 (final pH) by rapid mixing of $Fe(NO_3)_3$ and NaOH solutions at 298 K. The surface of the deposit is negatively charged: 5.77 [29] and 6.5 [30] PZC (point of zero charge) values are reported. To achieve adsorption of the negatively charged Au particles on the negatively charged FeO_x surface it was necessary to recharge the support surface to positive by adsorbing PDDA polycation [poly(diallyldimethyl-ammonium) chloride] as described in [27]. The sample was filtered, washed, dried at 355 K. In order to remove the organic impurities (tannin, citrate and PDDA), the sample prior to hydrogenation measurements was calcined in 10% O_2 at 663 K for 6 h. In a similar way the supporting FeO_x, further on S2, was prepared at pH 7.6, after filtering and drying it was calcined at 673 K for 4 h.

AuS3 precursor sample was prepared at ambient by co-precipitation in single step by rapid mixing the aqueous solution of $Fe(NO_3)_3$ and $HAuCl_4$ with aqueous solution of Na_2CO_3 at pH 7.7. The rapid hydrolysis of $Fe(NO_3)_3$ and $HAuCl_4$ at ambient resulted in the formation of a gold catalyst precursor supported on 2-line ferrihydrite (vide infra) which was our primary objective [25,31,32]. The product was digested only for 30 min at 298 K, filtered and washed with distilled water. The precursor was dried at 325 K for 6 h and then kept in a desiccator.

The gold catalysts (AuS1, AuS2 and AuS3) were re-calcined and hydrogen treated prior to characterization or catalytic measurements. The pre-treatments involved precisely controlled ramp (5 K min^{-1}) to maximum temperature, which was then maintained usually for 60 min in 10% O_2 and 30 min in 20% H_2. The notation (O673K/H473K) signifies calcining in 10% O_2 at 673 K for 60 min, cooling to ambient temperature and reducing in 20% H_2 at 5 K min^{-1} ramp and maintaining at 473 K for 30 min.

2.2. Characterization

The Au content of the iron oxide samples was determined by means of a double focusing inductively coupled plasma mass spectrometer (ICP-MS, ELEMENT2). The wt% of Au refers to Fe_2O_3 support composition. Surface area (BET) measurements were performed in a gravimetric system after vacuum treatment of the samples at 393 K for 1 h. Ex situ XRD measurements were carried out with a Phillips diffractometer using CuKα radiation source (λ = 0.15418 nm). The samples before removing from the reactor were He treated at 573 K, cooled to ambient and passivated in 300 ppm O_2/He. The XRD spectra were compared with those presented in JCPDS Data Files. The morphology and particle size distribution was determined by a Philips CM20 transmission electron microscope (TEM) operating at 200 kV equipped with energy dispersive spectrometer (EDS) for electron probe microanalysis. The surface composition of the catalysts was analysed by KRATOS XSAM800 XPS machine using Al-Kα source with 120 W X-ray power and 40 eV pass energy. TGA was performed in a Setaram gravimetric system in 20% H_2 at 5 K min^{-1} ramp. TPR was measured in a home-made device consisting of microreactor, temperature controller and quadrupole mass analyser (Pfeiffer Prisma QMS 200). The fingerprint spectra were recorded at 20 K min^{-1} ramp in 10% H_2.

2.3. Catalytic measurements

The hydrogenation activity was tested in a conventional single pass, flow reactor system consisting of reactor, furnace and temperature controller. In the investigations 70–200 mg catalyst was used. The inlet gas mixture contained 0.11% C_2H_2 and hydrogen in proportion H_2:C_2H_2 = 140, balanced with He. Rapid C2 separation was achieved with a 45/60 Carboxen-1000 column at 423 K (Supelco 1–2370). C4+ was measured with back-flash

Table 1
Chemical composition of Au/FeO_x precursor, surface area and gold particle size.

Samples	Au (wt%)[a]	Prep.[b]	Treatment (K)	Support	BET (m^2/g)	d_{Au} (nm)[c]
AuS1	4.55	DP	O673	Fe_2O_3[d]	9.2	3.5 ± 2.1
AuS2	3.02	SA	O673	Fe_2O_3	23	7.5 ± 2.8
AuS3	5.61	CP	O473	2LFh[e]	275	n.o.
S1	0	P	O673	Fe_2O_3[d]	9.2	–
S2	0	P	O673	Fe_2O_3	28	–

n.o.: not observed.

[a] Calculated from ICP-MS data for Fe_2O_3 support composition.

[b] DP, SA, CP and P stand for deposition precipitation, Au sol adsorption, co-precipitation, and precipitation, respectively.

[c] TEM measurements.

[d] Commercial Fe_2O_3 produced by Reanal, Hungary.

[e] 2LFh, 2-line ferrihydrite.