

# Selective Oxidation of Propylene to Propylene Oxide or Propionaldehyde over Au Supported on Titanosilicates in the Presence of H<sub>2</sub> and O<sub>2</sub>

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Gas phase selective oxidation of propylene to propylene oxide (PO) or propionaldehyde (PA) in the presence of H<sub>2</sub> and O<sub>2</sub> has been carried out with a propylene conversion in the range of 0.5-3.7% over gold deposited on titanosilicates by deposition-precipitation (DP) method; PO was obtained with a selectivity above 90% at the temperature range of 50 °C-120 °C whereas PA was obtained at temperatures higher than 200 °C with a selectivity above 70% over thoroughly washed catalysts with low Au loadings.

Direct gas phase epoxidation of propylene to PO using cheap oxidants like O<sub>2</sub> is one of the most important reaction not yet solved by catalysis<sup>1</sup>. Silver based catalysts used for ethylene oxide production from ethylene and molecular oxygen do not give promising activity in propylene conversion nor good selectivity for PO (< 60%). The conventional processes<sup>2</sup> for the production of PO need two reaction steps. The chlorohydrin process consumes hazardous Cl<sub>2</sub> and Ca(OH)<sub>2</sub>. The other process based on hydroperoxides produce either *t*-butyl alcohol or  $\alpha$ -methyl benzyl alcohol as co-products. We have reported earlier, for the first time, that epoxidation of propylene to PO takes place with a high selectivity (> 90%) over Au/TiO<sub>2</sub><sup>3</sup> and Au/Ti-MCM-41<sup>4</sup> catalysts. In this communication we would like to report our preliminary results on the gas phase selective oxidation of propylene over gold supported on a variety of titanosilicates.

The support, TiO<sub>2</sub> (P-25), was obtained from Degussa and was used as received. The supports TS-1<sup>5</sup>, TS-2<sup>6</sup>, Ti-beta<sup>7</sup> and Ti-MCM-41<sup>8</sup> were prepared according to the literature procedure using TPAOH (25% aq.), TBAOH (40% aq.), TEOH (40% aq.) and dodecyltrimethylammonium chloride (C12TMACl) as a structure directing organic templates, respectively, and were characterized by XRD, FT-IR and UV-vis spectroscopy and for their specific surface area measurements. In all the above titanosilicates absence of segregated crystalline TiO<sub>2</sub> (*ca.* 330 nm) anatase phase was confirmed by UV-Vis spectroscopy. A band between 200-250 nm has been assigned to isolated Ti atoms in tetrahedral (210 nm) and octahedral (230 nm) coordination. The deposition of gold on the supports was carried out by a deposition-precipitation (DP) method described previously<sup>9</sup>. The final catalysts were calcined in air at 400 °C for 4h. The amount of gold deposited on these supports was determined by inductively coupled plasma (ICP) technique. The mean diameter of gold particles was determined based on the observations of 50-400 particles using TEM (Hitachi H-9000). Propylene oxidation experiments were carried out in a fixed-bed quartz reactor (i.d. = 10 mm) using a feed containing C<sub>3</sub>H<sub>6</sub>, H<sub>2</sub>, O<sub>2</sub> and Ar, as a diluent, at a volume ratio of 1:1:1:7 and at a total flow rate of 33 ml.min<sup>-1</sup> (SV = 4000 cm<sup>3</sup>.g<sup>-1</sup>.h<sup>-1</sup>) passed over a catalyst (0.5 g) bed. The temperature was measured using a glass-tube covered Cr-Al thermocouple located in the center of the catalyst bed. The reactants and the products were analyzed by an on-line three GCs having TCD (AC and porapak Q columns) and FID (HR-20M column) detectors.

The preparation conditions, the actual Au loading and mean diameters of Au particles are shown for 9 different samples in Table 1. Table 2 show their performance in the propylene partial oxidation to PO and PA. Although Au deposited on anatase TiO<sub>2</sub> support always gave propylene oxide irrespective of the washing of the precipitate, in the case of titanosilicate supports the performance of gold catalysts in propylene oxidation is very much dependent on the washing of the precipitate. The DP method can not deposit gold on SiO<sub>2</sub> gel and MCM-41, suggesting that gold is deposited only on Ti sites in titanosilicates. Since the amount of isolated Ti sites in all the titanosilicates is limited to about 1-3% beyond which Ti segregates forming anatase and/or amorphous TiO<sub>2</sub> phase<sup>10</sup>, the amount of Au that can be deposited on these supports should be much smaller than that on TiO<sub>2</sub>. The actual gold loading of washed catalyst samples are very small for titanosilicate supports in comparison with that for TiO<sub>2</sub>, especially for TS-2 and Ti- $\beta$  zeolite (Table 1). Since the interaction of Au(OH)<sub>3</sub> with the isolated Ti sites may be weak, washing of the precipitate before drying should result in the dissolution of Au(OH)<sub>3</sub> deposited on titanosilicates.

The formation of PO primarily depends on the amount of Au loaded on these supports and its particle size. Because the formation of PA at high temperature was observed only with the thoroughly washed catalysts having very low Au loading (Table 1), its formation may be correlated to the presence of Brönsted acid sites in titanosilicates where PO can be transformed into PA. The catalysts which give good conversions and selectivity for PO at low

**Table 1.** Preparation (DP) conditions and characterization of gold supported on TiO<sub>2</sub> and titanosilicates

S	Support	Si/Ti ratio	Surface area (m <sup>2</sup> .g <sup>-1</sup> )	Au (in soln) (wt.%)	Au (By ICP) (wt.%)	D <sub>Au</sub> <sup>a</sup> (nm)
A	TiO <sub>2</sub>	0	45	1	0.67	3.4
B	TS-1	32	469	8	0.17	5.2
C	"			8	0.84	3.8
D	TS-2	30	333	8	0.03	3.6
E	"			8	0.04	2.1
F	Ti-beta	78	518	8	0.04	4.4
G	"			8	0.12	3.4
H	TiMCM41	100	1096	8	0.25	2.2
I	"			8	1.37	2.0

S= Catalyst sample; samples A, B, D, F and H were washed thoroughly with distilled water (5-7 lit./g support) before calcination. <sup>a</sup>A deviation of  $\pm 1-3$  nm is observed.

**Table 2.** Propionaldehyde formation from propylene catalyzed by supported gold catalysts using H<sub>2</sub> and O<sub>2</sub>

Catalyst composition	Code No.	Reaction temp (°C)	Conversion (%) of		Selectivity (%) for products				
			C <sub>3</sub> H <sub>6</sub>	H <sub>2</sub>	Acetaldehyde	Propylene oxide	Propionaldehyde	Acetone	CO <sub>2</sub>
Au/TiO <sub>2</sub> (P-25)	A	50	0.46	13.2	0	95	0	2.0	3
Au/TS-1	B	200	0.57	21.2	3.5	3.5	73.7	0	12
		250	1.84	37.9	8.2	1.1	68.5	0	13
		300	3.58	50.4	10.9	0	64.0	0	12
		350	3.71	54.8	9.2	0	60.5	0	17
Au/TS-1	C	100	0.71	7.9	1.0	93	0	1.0	5
Au/TS-2	D	200	0.45	19.9	6.7	0	33.3	4.4	47
		250	1.55	42.7	13.2	0	30.8	1.3	44
		300	2.81	69.9	13.5	0	16.7	6.8	49.1
Au/TS-2	E	100	0.68	5.8	2.0	91	0	3.0	4
Au/Ti-beta	F	200	0.22	7.9	4.5	3.7	68.2	0	18.2
		250	0.67	16.8	11.9	0	53.7	0	25.4
		300	1.22	34.8	14.8	0	34.4	0	36.1
		350	1.56	56.8	10.9	0	17.9	6.4	50
Au/Ti-beta	G	100	0.68	16.4	1.0	98	0	0	1
Au/Ti-MCM-41	H	160	0.46	37.8	4.3	0	41.3	8.7	39.1
		200	1.08	64.2	6.5	0	38.0	5.6	42.6
		250	1.79	78.4	8.9	0	29.1	6.1	47.5
Au/Ti-MCM-41	I	100	1.71	29.6	1	94	1.0	2.0	2

Note: Samples A, B, D, F and H were washed thoroughly with distilled water.

temperature are not selective for propionaldehyde at higher temperature but give CO<sub>2</sub> as the main product probably due to the presence of residual contaminants like Na<sup>+</sup> and Cl<sup>-</sup> ions in these unwashed samples. Also, over high Au loading catalysts which are relatively free from any residual contaminants (thoroughly washed catalysts e.g. 1.03 wt.% Au/Ti-MCM-41 with Ti/Si = 3/100) the successive oxidation of PA to CO<sub>2</sub> readily takes place at high temperatures (≥ 150°C). Thus, only the catalysts having very low Au loading (≤ 0.2 wt%) and relatively free from any residual contaminants are selective towards PA formation. In the propylene partial oxidation to PO, the maximum conversion of about 1.7% was obtained over Au/Ti-MCM-41 at 100 °C; the PO selectivity above 90% was observed on all the catalysts studied. Whereas, in propylene to PA reaction a maximum conversion of about 3.7% was obtained over Au/TS-1 with a PA selectivity greater than 70%. The formation of PO over Au/TiO<sub>2</sub> may take place via formation of hydroperoxo- or peroxo-like species as an intermediate involving both Ti and Au atoms as reported earlier<sup>12</sup>. It is likely that the deactivation is caused by oligomerisation of reaction intermediates and products.

In conclusion, this communication reports the gas phase selective oxidation of propylene to PO over finely dispersed gold supported on titanosilicates. With all types of titanosilicates as support for gold, a conversion of propylene of the order 1-2% with > 90% selectivity for PO were obtained when Au catalysts were not washed completely and/or having higher Au loadings. Gold deposited on titanosilicates with thoroughly washed precipitate having Au loading ≤ 0.2 wt% and relatively free from any residual contaminants gives propionaldehyde at higher temperature (≥ 200

°C) probably via PO as an intermediate.

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