Ring-opening reactions of propylene oxide (methyloxirane) over Au/MgO and unsupported Au catalysts

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The ring-opening reactions of propylene oxide (methyloxirane) were studied over an Au/MgO catalyst and Au powder at various temperatures in a pulse microreactor. The supported catalyst was significantly more active, and its activity was dramatically influenced by the method of pretreatment. When it was finished with hydrogen, conversion values were always above 70%, but often it was in the 90%+ range. The major reaction pathways were deoxygenation and isomerization. The comparison in the behavior of Au/MgO and Au powder pointed to the crucial importance of the support–metal interface in oxygen traffic and as a landing place for hydrogen-rich residues being the hydrogen source for water and alcohol formation (hydrogenation).

KEY WORDS: propylene oxide; Au/MgO and Au catalysts; ring-opening reactions; temperature dependence; role of support–metal interface.

1. Introduction

Not too long ago, gold was considered to be a hardly useful catalyst, a slightly active or completely inactive one in most of the industrially or academically important reactions. It was applied in mechanistic research, though, as a diluent of the transition metal cluster, studying ensemble effects [1]. Some 25 years ago, however, it started a career, which is skyrocketing these days [2]. It was found that gold was a very efficient catalyst in the oxidation reaction of CO even at subzero temperatures [3]. Many studies appeared and are still appearing concerning this catalytic system; thus, a lot of information is available on every aspect of this reaction (for reviews, see refs. [4,5]). The application of gold for catalyzing other reactions is still out of sight of researchers. A few other reactions were investigated [6] and some of them cannot be considered to be genuinely gold-catalyzed. The peroxidation of propylene by H_2O_2 over Au/TiO_2 is such an example [7]. In this system titania plays a crucial role in activating the double bond by forming surface alkoxide species and the role of gold is providing the oxygen from the dissociation of H_2O_2.

In this work, results concerning the reverse reaction (*i.e.* ring opening of the epoxide ring in propylene oxide) over unsupported and MgO-supported gold are reported. Earlier, this metal was not even thought to be worthwhile to try in this reaction; rather, various transition metals [8,9] and copper [10] were studied in hydrogenative transformations. Even the transition metals did not display superior activity and they were hardly active, if at all, without added hydrogen. To our surprise Au/MgO proved to be active in ring opening even without added hydrogen. However, it also became clear that the support plays a crucial role here, similarly to the above-mentioned epoxidation reaction, but not in the same manner.

2. Experimental

Methyloxirane (MOX) was a commercially (Fluka) available compound (racemic mixture was purchased) and was used as received. Hydrogen was produced in a Matheson generator. The high-purity nitrogen contained less than 0.0001% contamination.

MgO (99+%, BET: 155 m^2/g) and gold chloride hydrate (50% Au) and gold powder (99.9+%, 1.5–3.0 μm in size) were the products of Fluka-Aldrich Chemical Co.

The 3% Au/MgO catalyst was prepared by the adsorption of gold chloride hydrate. The MgO powder was suspended in distilled water (where it was hydrated partially), stirred, and added under vigorous stirring to an aqueous solution of $HAuCl_4 \cdot xH_2O$ at room temperature. After filtration the solid was resuspended and washed three times with 100 cm^3 portions of distilled water, and dried overnight at 70 °C in a vacuum oven. The basicity of the partially hydrated magnesia appeared to be adequate for the complete hydrolysis/adsorption of the gold-containing salt as the analysis of the residual solution revealed. Various kinds of treatments were applied on samples of the dried catalysts at 623 K: (i) 1 h of calcination in air, He stream (45 cm^3/min) for 1 h, (ii) H_2 stream (45 cm^3/min) for 1 h, (iii) 1 h of calcination in air, H_2 stream (45 cm^3/min) for 1 h, (iv) 1 h of calcination

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in air, H_2 stream (45 cm^3/min) for 1 h, He stream (45 cm^3/min) for 1 h. The aims of these treatments were to dehydrate the support, to complete the decomposition and reduction of the gold precursor and to generate defect sites on the support and presumably at the gold–support interfaces.

The catalyst was characterized by scanning electron microscopy (SEM) (JEOL 6300F instrument) and transmission electron microscopy (TEM) (Philips CM-300 FEG instrument).

The reactions of methyloxirane were studied in a pulse reactor system applying He as carrier (45 cm^3/min gas flow). The reaction temperature was varied in the 363–473 K range. The size of the pulse was 1 μL and 10 mg of catalyst was used. The following pulse sequence was applied for each catalyst: three consecutive pulses at 363 K, then a pulse at 393, 423 and 473 K, respectively; 30 min was allowed to elapse between the pulses. At 363 K the reaction mixture composition after the third pulse is listed in table 1. Blank experiments (experiments without the catalyst and over the metal-free support) have been performed at the temperatures applied in catalytic experiments and no transformation of methyloxirane has been found.

Analysis of the product mixture of was done by an online GC-MS system (Hewlett-Packard (HP) 5890 gas chromatograph equipped with an HP 5970 quadrupole mass selective detector). Good separation was achieved on a 50-m long CPWAX 52CB coated CHROMPACK WCOT fused silica capillary column by applying a temperature program (303 K for 15 min, 323 K for 10 min and 473 K for 10 min). Product identification was based on the NBS/NIH/EPA/MSDC database, clean samples.

3. Results

3.1. The Au/MgO catalyst

Since ambiguities do exist on the hydrogen, oxygen or CO chemisorption behavior of gold catalysts [6], the particle size of the Au/MgO catalyst was not estimated by titrating the surface gold atoms by these gases; rather, TEM and SEM measurements were applied.

Table 1

Composition of the reaction mixture in the ring-opening reactions of methyloxirane (MOX) over gold catalysts at increasing temperatures after various pretreatments (pulse system with 1 μL pulse size, 45 cm^3/min He as carrier, 10 mg catalyst)

T (K)	Composition (mol%)				
	MOX	C_3H_6	Acetone	2-Propanol	H_2O
Au/MgO (air: 623 K, 1 h, He stream: 623 K, 45 cm^3/min, 1 h)					
363	99.8	0.2	0.0	0.0	0.0
393	97.7	1.7	0.3	0.0	0.3
423	92.8	2.8	3.0	1.0	0.4
473	65.2	9.8	20.1	2.8	2.8
Au/MgO (H_2: 623 K, 45 cm^3/min, 1 h)					
363	0.0	100.0	0.0	0.0	0.0
393	1.2	90.9	7.9	0.0	0.0
423	24.4	40.6	28.8	1.3	4.9
473	29.1	20.3	43.6	2.4	4.6
Au/MgO (air: 623 K, 1h; H_2: 623 K, 45 cm^3/min, 1 h)					
363	4.0	96.0	0.0	0.0	0.0
393	7.9	70.3	18.6	1.8	1.4
423	6.9	36.1	46.1	4.8	6.1
473	4.6	18.5	61.4	6.5	8.8
Au/MgO (air: 623 K, 1h; H_2: 623 K, 45 cm^3/min, 1 h; He: 623 K, 45 cm^3/min, 1 h)					
363	98.9	1.1	0.0	0.0	0.0
393	93.4	6.5	0.0	0.0	0.1
423	73.2	13.8	8.4	3.3	1.3
473	36.7	22.4	23.5	12.9	4.5
Au powder (air: 623 K, 1 h; H_2: 623 K, 45 cm^3/min, 1 h)					
363	100.0	0.0	0.0	0.0	0.0
393	100.0	0.0	0.0	0.0	0.0
423	99.8	0.0	0.2	0.0	0.0
473	99.3	0.1	0.6	0.0	0.0
MgO (air: 623 K, 1h; H_2: 623 K, 45 cm^3/min, 1 h)					
473	100.0	0.0	0.0	0.0	0.0

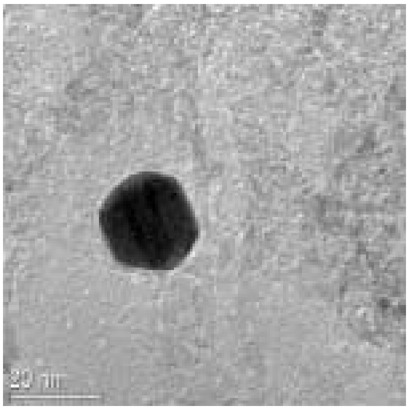

Figure 1. TEM image of a well-developed hexagonal gold particle of the 3% Au/MgO catalyst.

The idea turned out to be useful, since besides the expected hexagonal gold particles (a particularly well-developed representative is displayed in figure 1), to our knowledge, until now unseen, nanosize (some 200–300 nm in length) Y-shaped gold species were also observed (figure 2).

The average particle size (leaving out the Y-shaped and some extremely well-developed gold crystallites) was found to be 7.8 ± 3.1 nm.

3.2. The reactions

The ring-opening reactions of methyloxirane proceeded at temperatures as low as 363 K over Au/MgO catalysts, irrespective of the method of pretreatment. The main reaction at this temperature and at 393 K was deoxygenation, which requires the scission of both C—O bonds and the formation propylene. At 393 K the sum of acetone (the product of isomerization) and 2-propanol (the product of hydrogenative ring opening) concentration became comparable with that of propylene, and at 473 K it even surpassed that of the deoxygenation product. Desorbed water appeared in most cases at 393 K, although in very small quantities. Its concentration in most instances increased with increase in temperature. The compositions of the reaction mixtures following the reactions at each temperature are listed in table 1.

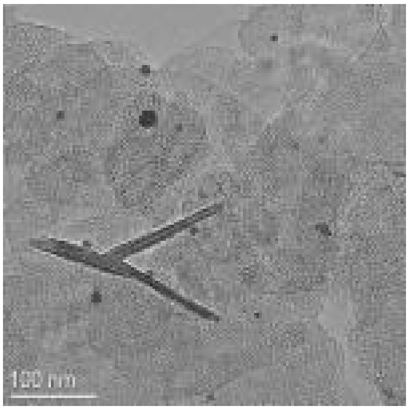

Figure 2. TEM image of a Y-shaped gold particle of the 3% Au/MgO catalyst.

It is to be seen that (i) MgO was not reactive and (ii) the Au powder was hardly active even at the highest temperature applied, (iii) when the transformation occurred over Au powder acetone was formed rather than propylene and, finally, (iv) pretreatment conditions exerted dramatic differences in the rate of methyloxirane transformations but not on product distribution.

4. Discussion

Since studies appeared in the literature covering the hydrogenative transformations of methyloxirane (the other reactant was hydrogen, for a review, see ref. [11]), and furthermore, over some transition metal catalysts the presence of hydrogen proved to be necessary to obtain desorbed ring-opening products, perhaps it should be explained why He was used as the carrier instead of hydrogen in this study. Although controversies exist, it seems to be common wisdom that gold does not readily adsorb hydrogen gas, if at all [6]. Therefore, we chose not to use hydrogen, but to see if reactions occur without it. Since methyloxirane transforms over silica-supported Ni, Pd and Cu without hydrogen, the attempt was not expected to be hopeless. Indeed, reactions did occur; moreover, depending on the pretreatment conditions, high activity was observed.

It appears to be clear that for achieving high conversion, pretreatment must be finished with hydrogen. When He was applied in the final stage of this procedure methyloxirane transformed slowly and was accelerated significantly (but never reaching the conversion level obtained over hydrogen-pretreated catalysts) only at 473 K.

Hydrogen pretreatment may have twofold effects. One is completing the reduction of the metal component and the other is creating new defect sites on the support, probably at or near the interface with the deposited gold species. Although the temperature of hydrogen treatment is not high enough for the substantial reduction of MgO, partial reduction, especially near the gold–support interface, may occur. It is known that doping MgO can make the formation of oxygen vacancies easier, while high-temperature hydrogen treatment anneals out the defect sites of (pure) MgO [12].

If there is no added hydrogen, one may not expect products containing extra hydrogen. However, at higher temperatures non-negligible 2-propanol and water formation was observed. The extra hydrogen should have been made available by the degradation of certain methyloxirane molecules (hydrogen-rich adsorbed carbonaceous deposits, possibly located at the gold–support interface), which might occur at higher temperatures. Indeed, hydrogenated products were not detected at all or were found in negligible amounts at lower temperatures. Hydrogenated products were not observed over Au powder either. This is an indication of the involvement of the support possibly at the support–gold interface.

As far as the source of oxygen for water is concerned oxygen detached from methyloxirane can spill over to the support (the driving force is filling up oxygen defects in the MgO crystal structure) and can shuttle back to the metal crystallites, especially at higher temperature. Thus, the support is essential for the catalytic activity beyond serving merely as a substrate for dispersing the gold particles [13].

5. Conclusions

An Au/MgO catalyst, containing hexagonal as well as Y-shaped gold species, proved to be active in the ring-opening reactions of propylene oxide. The reaction was mainly deoxygenation, but isomerization and at higher temperatures water as well as alcohol formation (hydrogenation) also occurred. Pretreatment conditions dramatically affected the activity of the catalysts. High activity could only be achieved when pretreatment was finished by hydrogen. The support was found to play an important role in accepting oxygen removed from methyloxirane by the metal and shuttling it back for water formation at higher temperature. The support–metal interface may serve the sites where hydrogen-rich methyloxirane residues can sit and these residues may provide the hydrogen for alcohol and water formation.

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