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RESEARCH NOTE

Vapor-Phase Selective Oxidation of Aliphatic Hydrocarbons over Gold Deposited on Mesoporous Titanium Silicates in the Co-Presence of Oxygen and Hydrogen

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The selective oxidation of hydrocarbons is one of the most important chemical processes to produce oxygenates (1) which are used as key intermediates in organic synthesis. The oxiranes are versatile products that easily undergo ring-opening reactions to form bifunctional compounds. For example, methyloxirane (propylene oxide, hereafter denoted as PO) is mainly used for producing urethane polyols and propylene glycol. Industrial producion of PO requires two-stage processes, using chlorohydrin or hydroperoxides. Since direct selective oxidation by the use of oxygen is difficult to achieve, several approaches have been undertaken to produce PO by oxidation with hydrogen peroxide over titanosilicate catalysts in liquid phase (2, 3). It is also known that Pd supported on titanosilicate (4) can produce PO by hydrogen peroxide generated *in situ* from oxygen and hydrogen. Recently, Hölderich *et al.* reported that Pd and Pt co-supported on titanosilicate yield PO up to 12% from propylene, oxygen, and hydrogen in liquid phase (5).

When gold is deposited as fine particles on select metal oxides, it has been found that the supported gold exhibits exceptionally high catalytic activity for many reactions (6, 7). Propylene oxide can be selectively produced by the direct vapor-phase oxidation of propylene in the copresence of oxygen and hydrogen using catalysts comprised of gold deposited on titanium dioxide (8).

New materials consisting of amorphous silica with regular pore structure, therefore called mesoporous molecular sieves MCM (Mobil Crystalline Materials) (9), exhibit an X-ray diffraction pattern with at least one peak at a d-spacing greater than about 18 Å with a relative intensity of 100. Among them, MCM-41 consists of a regular, hexagonal array of uniform channels with each pore surrounded by six neighbors. Isomorphous substitution of Si by Ti has been attempted by performing the synthesis in the presence of titanium compounds. Titanium containing mesoporous materials Ti–MCM-41 has been tested for oxidation of hydrocarbons in liquid phase, using H_2O_2 or hydroperoxides as oxidants (10–12). Gold supported on Ti–MCM-41 is proved to be selective in the epoxidation of propylene in the copresence of O_2 and H_2 (13). Other related titanium silicates can also work as an effective support for gold in the selective oxidations of propylene (14, 15).

In continuation, we now investigate to compare the catalytic behavior of gold deposited on Ti–MCM-41 and gold deposited on TiO_2 dispersed on silica for the epoxidation of propylene. An attempt was also made by using Au/Ti–MCM-41 catalysts to selectively oxidize propane to acetone and isobutane to *t*-butanol with a H_2–O_2 mixture in flow conditions.

The MCM-41 samples were synthesized by using dodecyl trimethyl ammonium chloride as a template, following the procedure described in (10). Ti–MCM-41 supported gold catalysts were prepared by deposition–precipitation (DP) of $Au(OH)_3$ (16) on Ti–MCM-41 with analyzed ratios of $Ti/Si = 2.0/100$; 2.8/100; 4.8/100 at pH 7 in an aqueous solution of $HAuCl_4$. After filtration, the precursors were washed with 500 ml water, dried, and calcined in air at 673 K for 4 h. The Ti/Si ratio and the actual gold loadings deposited on the supports were determined by ICP (inductively coupled plasma) analysis. Since gold hydroxide cannot be deposited at low pH, the DP method is useless for metal oxides having low point of zero charge; for example, SiO_2. On pure silica MCM-41 gold was deposited by the grafting of an organogold complex in vapor phase (GVP) (17). The particle size distribution was obtained by a transmission electron microscope (TEM) (Hitachi H-9000NA). TEM micrographs showed that gold particles were homogeneously dispersed on the support, with a mean diameter around

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2 nm. Au–TiO_2/SiO_2 and Au/TiO_2/Ti–MCM-41 catalysts were prepared by impregnating SiO_2(Fuji Davison, ID gel, specific surface area; 310 m^2/g) and Ti–MCM-41 with titanyl acetyl acetonate, respectively, followed by drying and calcination in air at 773 K. The TiO_2 loading was 1.0 wt% with respect to the supports.

The catalytic activity of the samples was measured in a flow reactor at atmospheric pressure over the temperature range of 323–393 K. The samples were sieved between 70 and 120 meshes (44–125 μm fractions) and weighed to 0.5 g. Catalysts were pretreated in a mixture of $O_2 : Ar$ (1 : 7) at 573 K for 1 h. A gaseous mixture of hydrocarbon, oxygen, hydrogen, and argon as diluent ($HC : O_2 : H_2 : Ar = 1 : 1 : 1 : 7$) was passed through the fixed bed containing a catalyst sample. The space velocity was 4000 ml/g · h. The reactor outflow was analyzed by means of a system composed of three gas chromatographs, two of them with TCD detectors using an active carbon column for H_2 and O_2 and a Porapack Q column for CO_2, H_2, and propane, one with a FID detector using a HR-20M capillary column for PO, CH_3CHO, $(CH_3)_2CO$, C_2H_5CHO, C_3H_6, and $CH_2{=}CHCHO$. The conversion of propylene was calculated based on the amount of products in the effluent gas.

Table 1 lists the amount of gold (in weight % to the support) in the starting solutions for the deposition–precipitation and the actual gold loadings. Higher contents of titanium in the supports result in larger amounts of gold actually deposited (see samples 1, 2B, and 3C), suggesting that gold is probably deposited on titanium sites in Ti–MCM-41.

TEM micrographs for the 2B catalyst (in Table 1) prior to and after reaction are presented in Fig. 1 (a, b). Since dodecyl trimethyl ammonium chloride was used as a template during the synthesis of Ti–MCM-41, the pore diameters of the samples are about 2.0–2.5 nm (18). Figure 1a shows that before reaction gold particles are homogeneously dispersed on the suppot with an average diameter around 2 nm . The particle size distribution (Fig. 1a) that about 30% of the gold particles have a diameter above 2.5 nm suggests that a fraction of gold particles deposited are not incorporated in the pores of the support. Figure 1b shows that these particles located outside the pores are coagulated during the reaction. However, the majority of gold particles are encapsulated in the channels of the Ti–MCM-41 and they are prevented from coagulation and from irreversible deactivation.

TABLE 1

The Amount of Titanium and Gold in the Catalyst Samples Tested

No.	Ti/Si molar ratio	Gold loading wt% Solution	Gold loading wt% Actual
1	2.0/100	8	1.10
2A	2.8/100	4	0.92
2B		8	1.20
2C		12	1.70
3A	4.8/100	2	0.61
3B		4	1.81
3C		8	2.60

Figure 2 shows typical results for the reaction of hydrocarbons with hydrogen and oxygen over Au/Ti–MCM-41 catalysts at 373–393 K. The best catalytic performance in this reaction was obtained with the 2B sample (8 wt% Au loading in solution and actual Au loading of 1.2 wt% on Ti/Si = 2.8/100). The partial oxidation products, PO from propylene, acetone from propane, and *t*-butanol from isobutane, have been obtained with selectivities of 95, 48, and 85% at hydrocarbon conversions of 1.8, 0.3, and 2.2%, respectively. These products are the same as those obtained with Au/TiO_2 catalysts (19). A catalyst with the same gold loading on Ti-free silica MCM-41, prepared by GVP, was inactive. The Ti–MCM-41 (2.8/100) sample without gold loading was also inactive under these reaction conditions. This means that both components, gold and titanium, are indispensable to the selective oxidation of aliphatic hydrocarbons.

Figure 3 shows that in the oxidation of propylene over the 2B catalyst, a relatively long induction period of about 1.5 h is observed in propylene conversion at 373 K, whereas selectivity to PO and hydrogen conversion reach a steady state much earlier. The induction period becomes longer at 323 K. The consumption of hydrogen is about double that over Au/TiO_2/SiO_2 for a similar conversion of propylene, suggesting that selective oxygen species formed by the reaction of oxygen with hydrogen may have a smaller chance to react with propylene. Since Ti cations are isolated from each other in Ti–MCM-41, the long induction period can be regarded as a period which is necessary to accumulate selective oxygen species, probably H_2O_2, on the Ti–MCM-41 surface and in the gas phase. Another probability is that PO formed first remains on the Ti–MCM-41 surface until saturation and then tends to desorb from the surface.

Figure 4 shows PO yield over 8 wt% (in solution) Au/1 wt% TiO_2/SiO_2 as a function of time. The catalytic activity of this catalyst monotonically decreases with time. Water is continuously formed during the oxidation of propylene, and the oxygenated intermediates may block the active sites and depress the adsorption of hydrocarbon on the surface of the catalyst. On the other hand, MCM materials have hydrophobic nature and Ti–MCM-41 preferentially adsorbs olefin molecules which are less polar. This may suppress the competitive adsorption of water and probably avoid the accumulation of the oxygenated intermediates resulting in more stable catalytic activity.

Taking into account the experimental results obtained in the present and previous works (8), the following reaction

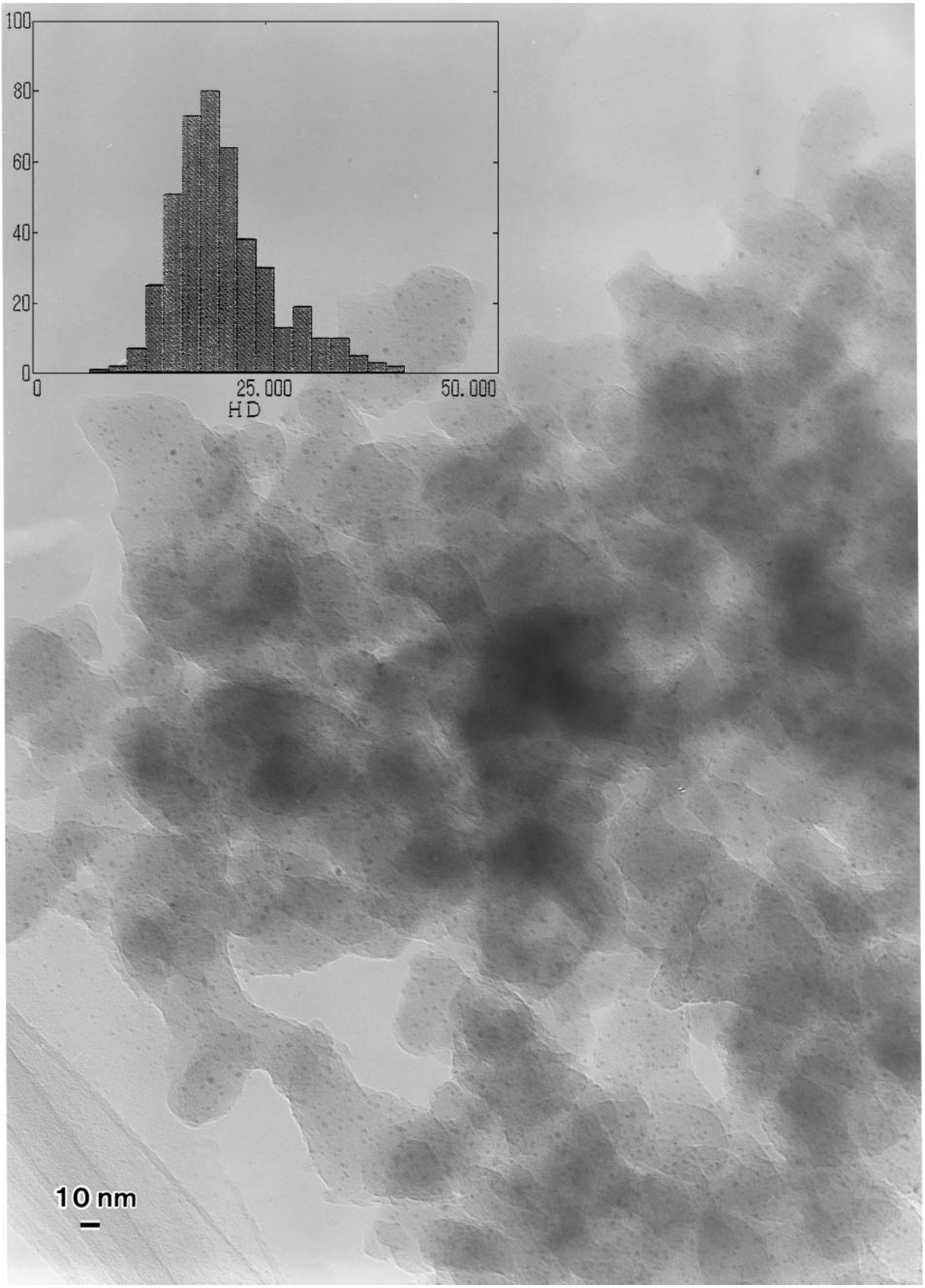

FIG. 1. TEM photographs of Au(1.2 wt%)/Ti–MCM-41(Ti/Si = 2.8/100) catalyst (No. 2B in Table 1) (a) Before reaction and (b) after reaction. The size distribution of Au particles is shown, with the number of Au particles as ordinate and the diameter as abscissa.

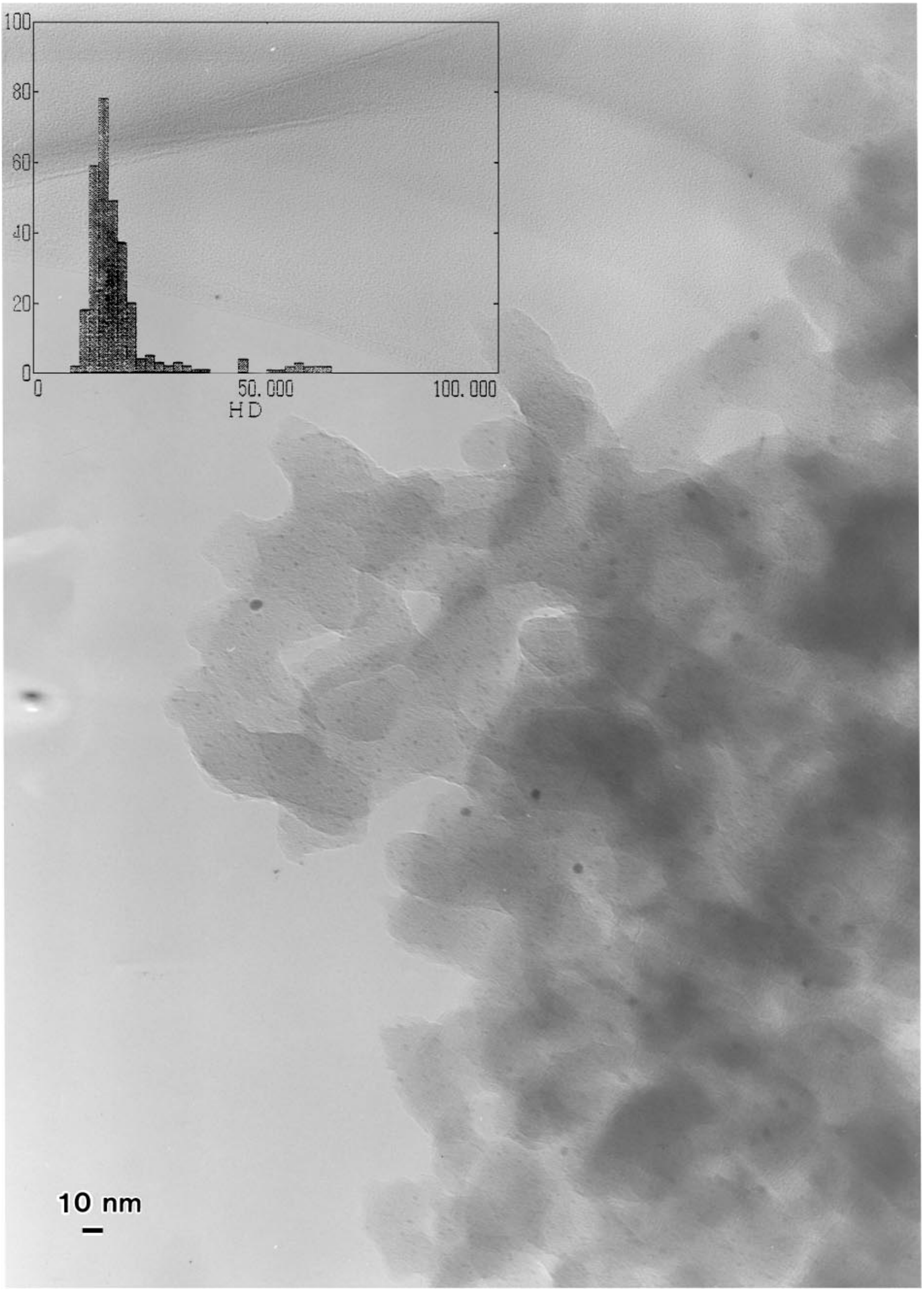

FIG. 1—*Continued*

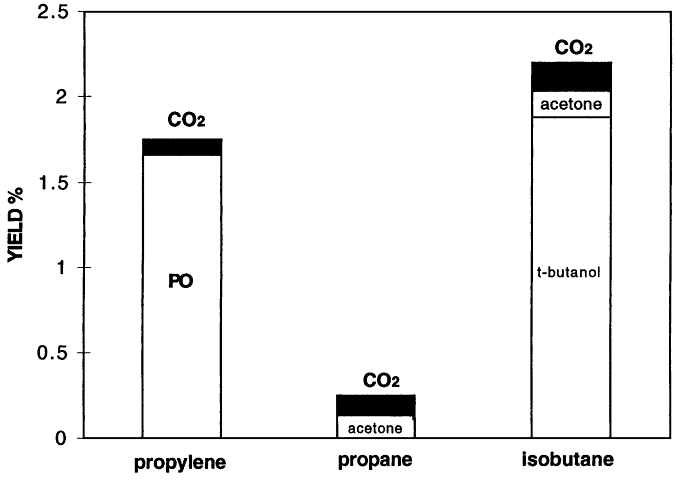

FIG. 2. Yield of products in the oxidation of propylene at 373 K, propane at 393 K, and isobutane at 393 K on the catalyst 2B (see Table 1) in the presence of oxygen and hydrogen.

pathways may be proposed: Hydrocarbon covers partly the surface of Au particles, over which H_2 reacts with O_2 to form H_2O_2 and H_2O. H_2O_2 formed is transmitted to the free titanium sites on the surface of Ti–MCM-41 and there it is transformed to hydroperoxo-species. Hydrocarbon adsorbed on the surface of Ti–MCM-41 reacts with the hydroperoxo-species to yield oxygenates.

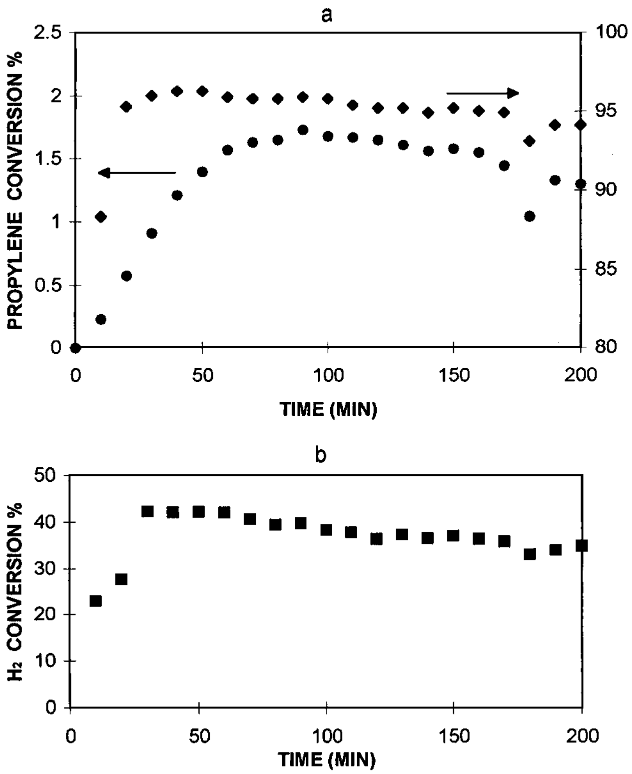

FIG. 3. Time course of propylene conversion and selectivity to PO (a) and hydrogen consumption (b) at 373 K over the catalyst 2B (see Table 1).

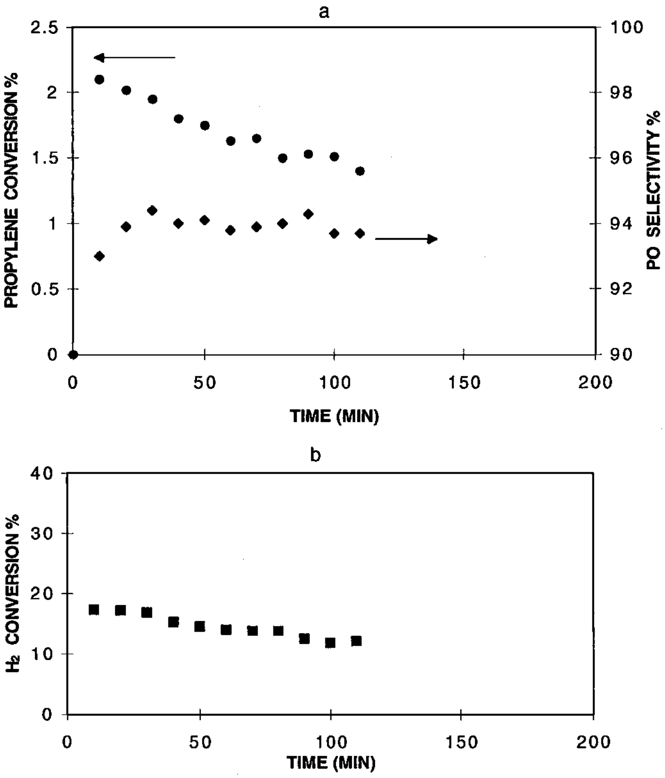

FIG. 4. Time course of propylene conversion and selectivity to PO (a) and hydrogen consumption (b) at 373 K over Au(8 wt% in solution)/(1 wt%)TiO_2/SiO_2.

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