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Gold(III) – metal organic framework bridges the gap between homogeneous and heterogeneous gold catalysts

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ABSTRACT

A MOF containing an Au(III) Schiff base complex lining the pore walls has been prepared by a post-synthesis method. The Au(III)-containing MOF is highly active and selective for domino coupling and cyclization reactions in liquid phase, the Au(III) species remain after the reaction, and the catalyst is fully recyclable. This gives higher activity than homogeneous and gold-supported catalysts reported up to now.

The well-defined Au(III) sites are active for dissociating H_2 and proved to be active for the gas-phase selective hydrogenation of 1,3-butadiene into the butenes.

1. Introduction

The interest on the catalytic chemistry of gold has undergone a marked increase in recent years [1]. Supported gold nanoparticles and gold salts/complexes are the basis of the present gold rush in heterogeneous and homogeneous catalysis, respectively [1,2]. While catalyst recovery and process work-up are much easier in the case of solid gold catalysts in comparison with gold salts/complexes [3], it becomes more difficult to know the exact nature of the active sites associated with gold, and there is still an intensive debate on the nature of the gold species involved in the reaction and the potential role played by the support [1a,2a,2b]. It is not then surprising that research efforts are being made today to bridge the gap between homogeneous and heterogeneous gold catalysis [3a].

In the last years, a class of porous metal organic frameworks (MOFs) have aroused great interest for their potential application in gas separation and storage, sensors, and catalysis [4]. These materials are formed by metal ions or clusters acting as nodes and polyfunctional organic ligands as linkers. Unlike other materials (such as metal oxides), the lack of non-accessible bulk volume and the fully exposed metal sites in metal organic framework compounds provide an ultimately high degree of metal dispersion. However, if the coordination sphere of the metal ions is completely blocked by the organic linkers, then there are not free positions available to interact/activate with the reactants and this could limit the possibilities of MOFs for catalysis. Nevertheless, different strategies can be adopted in order to prepare MOFs with open metal sites [5,6]. One strategy [5a,5b] consists in using labile ligands in the synthesis of the MOF, that can be removed during the activation stage prior to the catalytic reaction. In most cases, the labile ligands are solvent molecules that expose a free coordination position when removed. Kitagawa and co-workers [5c] proposed an alternative approach to prepare MOFs with open metal sites, by using a pre-assembled metalloligand that can be further reacted with a second metal acting as a node in the framework.

Very recently, a new preparative strategy [6] consisting of the covalent post-synthesis modification of an existing MOF with suitable functional groups has been proposed, as opposed to the "pre-synthesis" strategy used so far. Wang et al. [6a,6b] described the modification of the amino groups of IRMOF-3 with alkyl anhydrides. This idea was later used by Costa et al. [6c] to prepare a MOF containing Gd(III) and 2-aminoterephthalate ligands. The amino group of the organic ligand was modified post-synthesis with two different functionalities, by reacting either with an isocyanate or with a carboxylic acid. Post-synthesis modifications of MOFs have also been applied very recently in different scenarios. Ingleson et al. [6d] described the preparation of a material containing Brønsted acid sites by post-synthesis protonation of the carboxylate ligands of a MOF with anhydrous HCl. Hwang et al. [6e] described the grafting of an amine pendant group to the chromium sites of the chromium terephthalate MIL-101, using a 1,ω-diaminoalkane. Morris et al. [6f] modified zeolite imidazolate frameworks (ZIFs).

During the preparation of this manuscript, a new work by Ingleson et al. [6g] has appeared describing the preparation of a material obtained by reacting the $-NH_2$ groups of IRMOF-3 with

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salicylaldehyde to form the corresponding imine. The authors used this ligand to complex metal ions, as demonstrated by covalently anchoring vanadyl acetylacetonate. This material was found to be active for the oxidation of cyclohexene with ^{t}BuOOH, but the turnover frequencies obtained were low and the material was found to loose its framework integrity [6g].

In a parallel approximation, we have also used the covalent post-synthesis methodology to prepare MOFs with open metal sites with potential use in catalysis. We have prepared a MOF containing a Au(III) Schiff base complex lining the pore walls. We have anticipated that if coordinative unsaturated gold ions (i.e., open cationic gold sites) can be created in MOF, the resulting heterogeneous gold catalyst would emulate the catalytic properties of homogeneous counterparts, i.e. well-defined active sites with dispersed metal ions. It is presented here that the resulting MOF containing gold is a highly active, selective, and reusable catalyst for domino coupling and cyclization reactions in liquid phase, and hydrogenation of 1,3-butadiene in gas phase. To the best of our knowledge, this material represents the first example of a catalytically active MOF containing isolated cationic gold species, and has allowed to set the discussion on the nature of the gold active sites for selective diene hydrogenation. It represents a novel catalyst that helps to bridge the gap between homogeneous and heterogeneous catalysis [7].

2. Materials and methods

The detailed preparation and characterization of IRMOF-3-SI-Au, Au/ZrO_2, and the homogeneous Au(III) Schiff complex catalysts is given in the Supporting Information.

2.1. Catalytic reactions

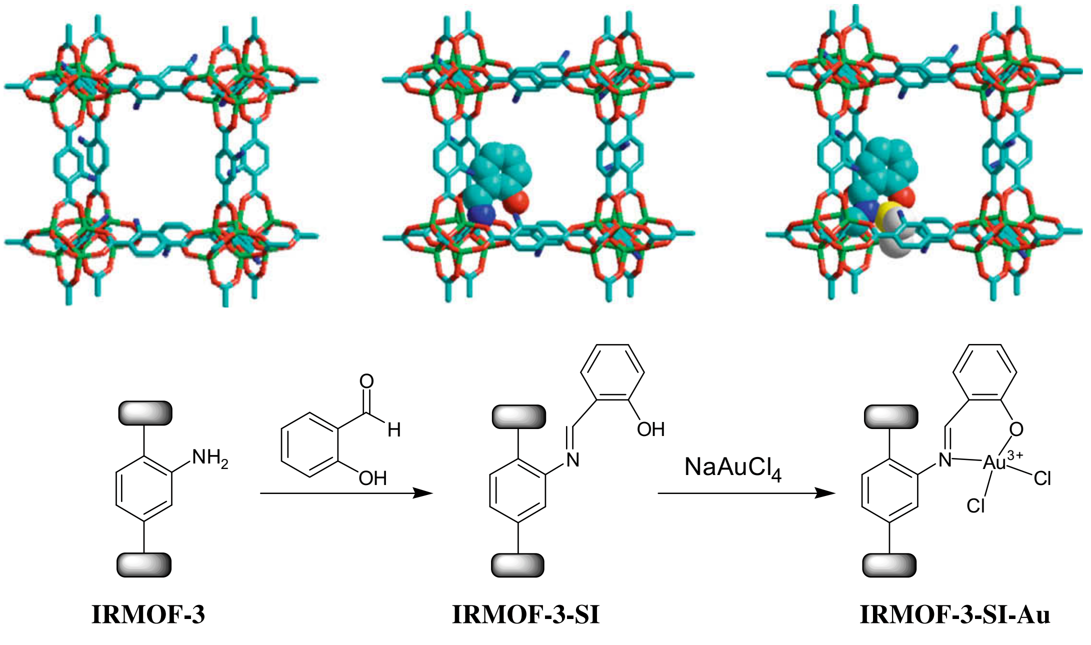
Three-component coupling and cyclization of N-protected ethynylaniline, amine, and aldehyde: All reactions were performed in a closed glass reactor (2.0 mL, SUPELCO) with vigorous stirring (ca. 1000 rpm) at 40 °C (or 80 °C). The gold catalyst of desired weight was added to a mixture of N-protected ethynylaniline (0.20 mmol), amine (0.24 mmol), and aldehyde (0.40 mmol) in 1.0 mL of 1,4-dioxane with n-octane as an internal standard. The pure product was obtained by flash chromatograph and identified by GC-MS and ^{1}H NMR, ^{13}C NMR (see Supporting Information).

Selective hydrogenation of 1,3-butadiene: Hydrogenation of 1,3-butadiene was performed in a fixed-bed quartz reactor (i.d.= 6 mm) at atmospheric pressure and 130 °C. The reactants of 2.0 vol% 1,3-butadiene in H_2 (13.0 mL min^{-1}) and Ar (28 mL min^{-1}) were introduced to the catalyst (containing 0.0011 mmol gold, diluted with 450 mg SiC), Specifically, the Au/TiO_2 catalyst was in situ pretreated in flowing Ar at 130 °C or H_2 at 250 °C, respectively, before reaction. The reactor effluent was in situ analyzed using gas chromatograph (FID, a HP-PLOT/Al_2O_3 capillary column).

3. Results and discussion

3.1. State of gold and stability in the gold MOF IRMOF-3-SI-Au

The starting material chosen for this study was IRMOF-3 [4b], since the presence of NH_2 groups allows for the easy covalent modification. The material was synthesized at room temperature, following a modification of the procedure described by Huang et al. [8] using 2-aminoterephthalic acid (H_2ATA) instead of terephthalic acid. The material was washed with chloroform prior to post-synthesis modification to remove occluded DMF solvent molecules. A freshly prepared sample was contacted for a short time at room temperature with a chloroform solution containing salicylaldehyde, which causes a color change from cream to light or deep yellow (depending on the loading of salicylaldehyde). The color change is accompanied by a new UV–Vis absorption band at 450 nm (Fig. S1) and a new ^{13}C NMR band at 167 ppm due to the C = N (Fig. S2), which are indicative of the formation of the corresponding salicylideneimine. This sample will be hereafter referred to as IRMOF-3-SI. The contact time of this reaction is important, since it was observed that for contact time longer than ca. 0.5 h the material obtained had a very low crystallinity (Fig. S3). The final step to prepare the Au(III)-containing material, IRMOF-3-SI-Au, consisted in reacting a suitable gold precursor, $NaAuCl_4$, with the



Scheme 1. Post-synthesis modification procedure for obtaining MOFs containing Au(III) Schiff base complex. Zn: green; O: red; C: light blue; N: deep blue; Au: yellow; Cl: white. H atoms are omitted. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

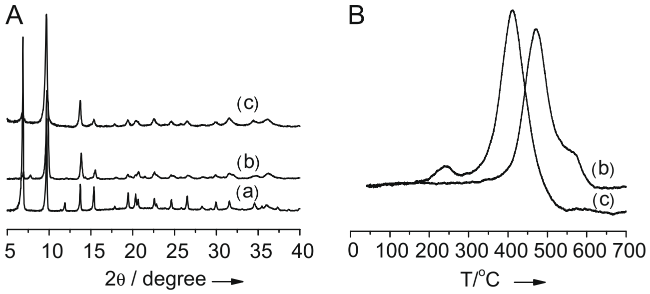


Fig. 1. (A) X-ray diffraction patterns and (B) hydrogen temperature programmed reduction of samples IRMOF-3 (a), IRMOF-3-SI (b), and IRMOF-3-SI-Au (c).

imine-modified material. The preparative procedure is summarized in Scheme 1, while a detailed description of each step is given as Supporting Information.

According to the elemental analysis of the samples, using this preparative method a maximum functionalization of about 3% of the total $-NH_2$ groups was produced without losing the framework integrity, while gold complexation by the Schiff base complex was almost quantitative. Increasing the degree of functionalization with salycilideneimine required longer contact times, but this caused a severe diminution of the crystallinity of the final material, as commented above. Thus, 3% functionalization is the best compromise we found between degree of functionalization and crystallinity. Nevertheless, since the ensuing gold complexation is quantitative, a 3% functionalization of the Schiff base allows introducing up to 2 wt% of gold in the material, which is a typical value for the metal loading of heterogeneous catalysts.

The N_2 adsorption-desorption experiments show a decrease in BET surface area from 750 to 400 $m^2\,g^{-1}$ after IRMOF-3 was modified by salicyladehyde, while the surface area remained practically unchanged after Au(III) complexation (380 $m^2\,g^{-1}$).

The XRD pattern (Fig. 1A) of IRMOF-3 corresponds to that of a crystalline material with the expected structure [4b]. After functionalization with the imine and ensuing complexation with Au(III), the structure integrity of the solid is preserved. XRD pattern of IRMOF-3-SI-Au remains unaltered when the material was heated up to 300 °C in air, demonstrating that IRMOF-3-SI-Au is thermally stable. TG-DTA analysis shows a first weight loss of about 9 wt% between room temperature and 150 °C, due to removal of chloroform and a small amount of remaining DMF, and a second weight loss due to combustion of the organic part of the framework of ca. 56 wt% between 340 and 550 °C (Fig. S4). The absence of a diffraction peak at $2\theta = 38.2°$ (Au [1 1 1]), and examination of the samples by TEM (Fig. S5) both exclude the occurrence of metallic gold particles within our detection limits.

Fig. 1B shows hydrogen temperature-programmed reduction (TPR) profiles of IRMOF-3-SI and IRMOF-3-SI-Au. The TPR profile of IRMOF-3-SI-Au features two hydrogen consumption peaks: one at low temperature (190–280 °C) and another at high temperature (300–550 °C), while only one peak associated to hydrogen consumption at high temperature (370–610 °C) is found for IRMOF-3-SI. The high temperature peak can be assigned to decomposition of the IRMOF-3-SI support. The low temperature peak is due to reduction of Au^{III} ions into Au^0 atoms. Since the moles of hydrogen-consumption is exactly 1.5 times the molar number of gold in the IRMOF-3-SI-Au (as determined by ICP-AES), this result indicates that all gold atoms are in a +3 oxidation state, with no detectable amounts of Au^0 species, as already deduced from the XRD and TEM analysis. It is very important to point out that the reduction temperature (ca. 239 °C) of Au^{III} ions in IRMOF-3-SI-Au is higher than that found for gold on nanocrystalline CeO_2 or on ZrO_2 (Fig. S6), which stabilize surface cationic gold species [9]. Therefore, according to the relatively high reduction temperature needed for reducing Au^{III} in IRMOF-3-SI-Au, we can conclude that cationic gold species are highly stabilized in the Schiff base complex within the framework of the MOF (Scheme 1).

3.2. The gold MOF catalyst for three component coupling and cyclization: comparison with homogeneous catalysts

The new class of heterogeneous IRMOF-3-SI-Au should then be of catalytic interest due to the presence of well-defined isolated Au(III) stable active sites, fully accessible to reactant molecules. Therefore we expect that this type of Au(III)-MOF catalyst could be a useful heterogeneous counterpart of the Au(III) salt catalysts used up to now as well as a new way for heterogenizing homogeneous gold complexes [3a,10]. We will show here that the IRMOF-3-SI-Au catalyst gives TOF as high as (or even higher than) Au(III) salt catalysts but, unlike the salts, without reduction/decomposition during the reaction. This is firstly shown by applying the IRMOF-3-SI-Au catalyst for multicomponent domino coupling and cyclization of N-protected ethylaniline, aldehyde, and amine, a reaction that is known to be catalyzed by Au(III) species [11].

The indole nucleus is one of the most ubiquitous heterocycle in nature and synthetic compounds with biological activities, and thus the development of new, efficient, and sustainable synthesis protocols is highly desired [12]. Recent developments on synthetic strategies are mainly based on transition-metal (e.g., Pd and Cu) working in homogenous phase [12]. Very recently we have reported an atom-economy approach for three-component coupling of alkyne, amine, and aldehyde through C–H activation [11], and one example of indole synthesis based on domino coupling and cyclization catalyzed by supported gold. It was shown there that only a fraction of the total gold species, i.e. only the Au(III), are active for these reactions. If this is true, the IRMOF-3-SI-Au catalyst should then give a higher activity per total amount of gold than any of the previously reported heterogeneous gold catalysts, and certainly more active than $AuCl_3$ that is easily and rapidly reduced/decomposed during reactions [3b,3c,3d,3e].

Fig. 2 shows the kinetic curves for IRMOF-3-SI-Au, Au/ZrO_2, $AuCl_3$, and a homogeneous Au(III) Schiff base complex used as reference [10c], for the domino coupling and cyclization reaction of N-tosyl protected ethynylaniline (E1), piperidine, and paraformaldehyde at 40 °C. It can be seen there that E1 conversion increases continuously up to 93%, 36%, and 38% over IRMOF-3-SI-Au, Au/ZrO_2, and Au(III) Schiff base complex, respectively, within 14 h, while a maximum conversion of ca. 60% was obtained with $AuCl_3$ over 6 h.. If one calculates the turnover frequency (TOF) from the initial reaction rates from Fig. 2 taking into account the total gold content of the catalyst, the values obtained are

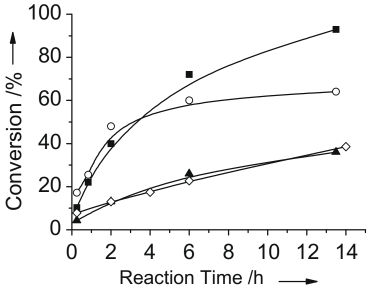


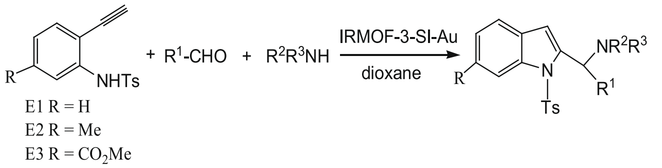
Fig. 2. Comparison of the catalytic activity over IRMOF-3-SI-Au (■, gold: 0.0008 mmol), Au/ZrO_2 (▲, gold: 0.0014 mmol), homogeneous Au(III) Schiff complex (◇, gold: 0.0008 mmol), and $AuCl_3$ (○, gold: 0.025 mmol) for domino coupling and cyclization of ethynylaniline (E1, 0.10 mmol), piperidine (0.12 mmol), and paraformaldehyde (0.20 mmol) with 1,4-dioxane (1.0 mL) as solvent at 40 °C.

52, 12, 40, and 3 h^{-1} for IRMOF-3-SI-Au, Au/ZrO_2, Au(III) Schiff base complex, and $AuCl_3$, respectively. The first conclusion from these results is that the IRMOF-3-SI-Au gives a much higher TOF than $AuCl_3$. Compared with the homogeneous gold(III) Schiff base complex, IRMOF-3-SI-Au gives a similar initial rate (52 vs 40 h^{-1}) but it is more stable, thus allowing to achieve higher conversions, and therefore higher turnover numbers (TONs). On the other hand, it is not surprising that the TOF of IRMOF-3-SI-Au is much larger than that of Au/ZrO_2 since it has been found that in the latter catalyst the fraction of Au^{III} with respect to total gold is only 0.25 [11]. However, if we consider the fraction of the cationic gold in Au/ZrO_2 to recalculate the TOF then the value obtained is 48 h^{-1}, which is not too different from the TOF measured with the MOF in which all Au^{III} species should be accessible and active. This comparison allows us to reach the following conclusions: (a) The cationic gold Au(III) species are the active sites for this reaction; (b) During reaction, cationic gold species are indeed stabilized in the IRMOF-3-SI-Au and Au/ZrO_2 catalyst, but they are less stabilized in the homogeneous Schiff base complex catalyst and $AuCl_3$ salt; (c) IRMOF-3-SI-Au with well-defined and accessible sites can, in practice, be a bridge between the homogeneous and heterogeneous gold catalysts, and can be used to bring additional light in the debate on the nature of gold species that are active on solid catalysts, as will be demonstrated later for the selective hydrogenation of 1,3-butadiene.

As we said before, and in contrast to the homogeneous Au(III) and Cu(I) salts [12c], the IRMOF-3-SI-Au catalyst can be successfully reused (100%, 99%, 95%, and 97% conversions were obtained after 3 h for four successive runs at 80 °C). Furthermore, the structural integrity of the material is basically preserved after the catalytic use (368 m^2 g^{-1}), in spite of some apparent crystallinity loss (Fig. S7). Both the absence of the [1 1 1] peak of metallic gold and the H_2-TPR on the reused catalyst show that reduction of Au(III) ions does not occur during the reaction, and the H_2 consumption of the reused catalyst still corresponds to exactly 1.5 times the total number of gold mols. The reusability of the material, together with the fact that the gold loading (as determined by ICP-AES) remained unchanged after the second cycle, excludes the occurrence of gold leaching from the solid to the liquid. Nevertheless, we have also carried out the so-called hot filtration test [4e,4f] to further demonstrate this point. The reaction in the presence of the IRMOF-3-SI-Au catalyst was allowed to proceed only to partial conversion (40% in 2 h) at 40 °C. At this point, the solution was quickly filtrated and the solids were removed. Then, when the filtrated was allowed to further react for 13 h, only an increase of 5.0% conversion was observed, which is due to the thermal reaction. (Fig. S8).

The IRMOF-3-SI-Au is a general catalyst for the three-component coupling and cyclization, as can be deduced by reacting various amines, aldehydes, and N-protected ethylanilines. The results summarized in Table 1 show that 90% of isolated yield can be obtained at 40 °C for the three-component coupling and cyclization of E1, paraformaldehyde, and piperidine (entry 1). Although the reactivity is a little lower when changing paraformaldehyde by cyclohexylcarboxaldehyde or octylaldehyde, good to excellent yields can still be obtained when the reaction was performed at 80 °C (entries 2 and 3). Remarkably the reaction with chiral amines was also successful, giving yields of more than 83% (entries 4 and 5). Ethynylaniline E2 bearing an electron-donating methyl group reacts smoothly with paraformaldehyde and cyclohexylcarboxaldehyde and gives yields of 94% and 83%, respectively (entries 6 and 7), while 78% and 70% yields are found with E3 bearing one electron-withdrawing methoxycarbonyl group (entries 10 and 11). Both E2 and E3 are allowed to react with chiral amines to afford accordingly coupling and cyclization products with good to excellent yields (entries 8, 9, and 12).

Table 1
Coupling of N-protected ethynylaniline, amine, and aldehyde catalyzed by IRMOF-3-SI-Au in dioxane.[a]



Entry	Ethynyl-aniline	R^1-CHO	R^2R^3NH[b]	*T* (h)	Yield (%)[c]
1	E1	$(HCOH)_n$	Piperidine	16	90
2	E1	Cyclohexyl	Piperidine	4	80
3	E1	Heptyl	Piperidine	6	95
4	E1	$(HCOH)_n$	M2	12	83
5	E1	$(HCOH)_n$	M3	6	91
6	E2	$(HCOH)_n$	Piperidine	16	94
7	E2	Cyclohexyl	Piperidine	12	83
8	E2	$(HCOH)_n$	M2	4	85
9	E2	$(HCOH)_n$	M3	4	92
10	E3	$(HCOH)_n$	Piperidine	12	78
11	E3	Cyclohexyl	Piperidine	12	70
12	E3	$(HCOH)_n$	M2	6	80

[a] Reaction conditions: ethynylaniline (0.2 mmol), aldehyde (0.4 mmol), and amine (0.24 mmol), IRMOF-3-SI-Au (14 mg, gold: 0.001 mmol), 1,4-dioxane (1.0 mL), 40 °C (80 °C for entries 2–5, 7–9, 11, 12).

[b] Chiral amines denoted as M2, M3 are (s)-(+)-2-(methoxymethyl)-pyrrolidine and (s)-(+)-2-methylpiperdine, respectively.

[c] Isolated yields based on ethynylaniline.

3.3. The gold MOF as catalyst for 1,3-butadiene hydrogenation: Elucidation of the active sites

As we said before, highly stabilized Au(III) species on MOF can help to elucidate the nature of the actives sites for particular reactions, especially in those cases where the reaction is performed under reducing atmosphere, and cationic gold species are claimed as the active sites. This is, for instance, the case for the hydrogenation of alkenes with gold catalysts. Indeed, it has been shown that supported gold catalysts are active for hydrogenation of alkenes and small metallic gold nanoparticles were assumed to be the active sites [13]. However, the suggestion was unconfirmed, and recently oxide-supported (MgO, ZrO_2) mononuclear Au(III) species [14] and isolated Au(III) ions [9c,9d,9e] have been claimed as the actual active sites for ethene and 1,3-butadiene hydrogenations, respectively. If this last hypothesis is true, i.e. isolated Au(III) ions are the active species for the selective hydrogenation of butadiene [9c], then our IRMOF-3-SI-Au catalyst with single, isolated Au(III) species should be active and selective for carrying out the hydrogenation of butadiene to butenes. If this was so, not only the hypothesis on the cationic nature of the active sites would be demonstrated, but also a new highly active heterogeneous IRMOF-3-SI-Au catalyst with well-defined and controlled active sites would be available.

Activity and selectivity over IRMOF-3-SI-Au for hydrogenation of 1,3-butadiene are shown in Fig. 3. For comparison, the results obtained over Au/TiO_2 catalyst (1.5 wt% gold) provided by World Gold Council pretreated either in flowing Ar at 130 °C, or in H_2 at 250 °C, have also been included. 1% 1,3-butadiene conversion was obtained in a blank test using gold-free IRMOF-3-SI.

The overall conversions for Au/TiO_2 catalyst pretreated in Ar and in H_2 were very similar (ca. 9%), and much lower than the conversion obtained over IRMOF-3-SI-Au (ca. 96%). The TOF (540 h^{-1}) for IRMOF-3-SI-Au calculated on the bases of total gold weight, is one order of magnitude higher than that of Au/TiO_2 catalysts (50.4 h^{-1}). Considering that Au/TiO_2 catalyst pretreated in Ar and

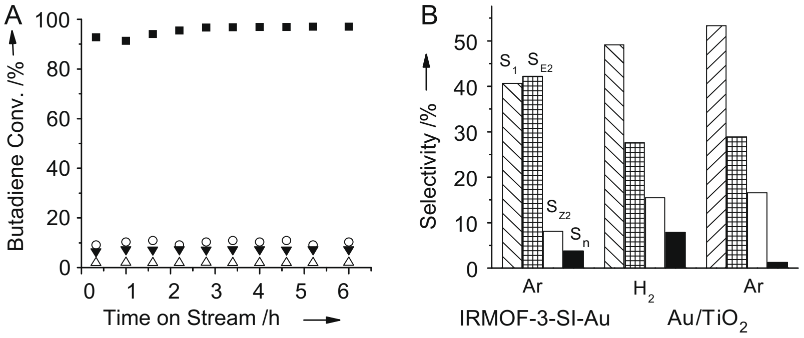


Fig. 3. (A) 1,3-Butadiene conversion versus time on stream and (B) product selectivity over IRMOF-3-SI (△), IRMOF-3-SI-Au (■), and Au/TiO_2 pretreated in flowing H_2 at 250 °C (○) and Ar 130 °C (▼) at 130 °C. S1, S_{E2}, S_{Z2}, and S_n represent the selectivity of 1-butene, E-2-butene, Z-2-butene, and *n*-butane, respectively.

H_2 both contain metallic gold, our results show that the oxidation state of gold is proven to be important for hydrogenation of 1,3-butadiene. The MOF-stabilized Au(III) species is more active than TiO_2-supported metallic gold. Interestingly, IRMOF-3-SI-Au shows very high selectivity (up to 97%) for butenes with 1-butene and E-2-butene as the main products, and only 3% of butane selectivity is detected at almost completely consumption of 1,3-butadiene. On the contrary, a significant amount of butane (ca. 8%) was formed on Au/TiO_2 pretreated in H_2 even at low conversion of 1,3-butadiene, and the butane selectivity sharply decreased for Ar pretreated Au/TiO_2 catalyst (Fig. 3b).

Since gold remains as Au(III) in IRMOF-3-SI-Au after the hydrogenation reaction, we confirm the previous suggestion that mononuclear Au(III) species [14] and isolated Au(III) [9c,9d,9e] are the active sites for ethane and 1,3-butadiene hydrogenation. This conclusion would be in agreement with the fact that homogeneous Au(III) Schiff base complex can activate H_2, and catalyzes the liquid-phase hydrogenation of diethyl itaconate in a batch reactor [10]. In the case of the MOF, we have now a solid catalyst with active surface-type Au(III) Schiff base complex that can activate H_2 and selectively perform the gas-phase hydrogenation of 1,3-butadiene. The clear advantage of the gold MOF catalyst with respect to MgO-supported mononuclear Au(III) species is that the latter are not stable in air and must be kept under anaerobic and anhydrous conditions [14], while IRMOF-3-SI-Au is stable in air and shows very stable activity for the selective hydrogenation of 1,3-butadiene (Fig. S9).

In conclusion a novel catalyst has been prepared by modification of a metal organic framework (IRMOF-3) with coordinative unsaturated Au(III) species based on a post-synthesis strategy. The resulting heterogeneous IRMOF-3-SI-Au catalyst exhibits high ability to stabilize cationic Au(III) species and 100% utility of gold active sites, which has emulated the catalytic properties of homogeneous gold catalysis. The IRMOF-3-SI-Au gives much higher catalytic performance in catalyzed domino coupling and cyclization of N-protected ethylanilines, amine, and aldehyde in comparison with oxide-supported gold and homogeneous gold salt/complex, and it has also demonstrated that Au(III) species are highly active and selective for the selective hydrogenation of 1,3-butadiene.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2009.04.021.

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