

Cu and Au Metal–Organic Frameworks Bridge the Gap between Homogeneous and Heterogeneous Catalysts for Alkene Cyclopropanation Reactions

Avelino Corma,^{*[a]} Marta Iglesias,^[b] Francesc X. Llabrés i Xamena,^[a] and Félix Sánchez^[c]

Dedicated to Professor José Barluenga on the occasion of his 70th birthday

Abstract: The copper and gold metal–organic frameworks (MOFs) [Cu₃(BTC)₂(H₂O)₃]_n, [Cu₃(BTC)₂] (BTC = benzene-1,3,5-tricarboxylate), and IRMOF-3-Si-Au are active and reusable solid catalysts for the cyclopropanation of alkenes with high chemo- and diastereoselectivities. This type of material gives better results than previous solid catalysts while working together with the homogeneous catalysts. These MOFs can help to bridge the gap between homogeneous and heterogeneous catalysis.

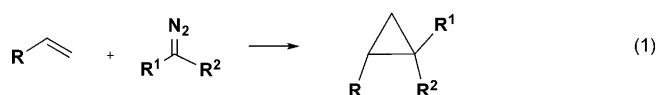
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Introduction

Metal–organic framework (MOF) materials are promising candidates as new heterogeneous catalysts due to their high surface area inside the pores and their tunable structure.^[1] An attractive feature of these solids is the presence of single-site active species in an identical environment within the crystalline matrix. Some applications of these porous materials, such as gas separation, gas storage,^[2a] and catalysis,^[2b–d] have already been described. Research into catalytic applications has mainly focused on rigid MOFs with permanent porosity and coordinatively unsaturated metal active sites that are accessible to the substrate.^[1d,3] Heterogeneous catalysis is one of the application areas in which MOFs could play an important role. Interest in introducing catalytic

properties into MOFs has increased recently^[4] because both metal ions or linkers can act as catalytic centers. Herein, we show that a copper-containing MOF [Cu₃(BTC)₂] (BTC = benzene-1,3,5-tricarboxylate) and a gold-containing MOF IRMOF-3Si-Au, with a gold(III) Schiff base complex that lines the pore walls,^[5] both give excellent activities and selectivities for alkene cyclopropanation reactions. We anticipated that if coordinative unsaturated gold ions (i.e., open cationic gold sites) can be created in MOFs, the resulting heterogeneous gold catalyst would emulate the catalytic properties of homogeneous counterparts, that is, well-defined active sites with dispersed metal ions.

One strategy employed in the synthesis of cyclopropane rings is based on the catalytic transfer of carbene fragments from diazo compounds to olefins.^[6] Transition metals from Groups 8 to 11 have been reported to decompose diazo compounds,^[7] and the carbene unit is later transferred to a variety of saturated or unsaturated substrates [Eq. (1)].^[8]



After the first reported use of a gold-based catalyst for the intermolecular carbene transfer from diazo compounds,^[9] very few other examples have been described based on this metal.^[10]

[a] Prof. A. Corma, Dr. F. X. Llabrés i Xamena
Inst. Tecnología Química, UPV-CSIC
Universidad Politécnica de Valencia
Consejo Superior de Investigaciones Científicas
Avda los Naranjos, s/n, 46022 Valencia (Spain)
Fax: (+34)963877809
E-mail: acorma@itq.upv.es

[b] Prof. M. Iglesias
Inst. Ciencia de Materiales de Madrid, CSIC
C/Sor Juana Inés de la Cruz 3
Cantoblanco, 28049 Madrid (Spain)

[c] Prof. F. Sánchez
Instituto de Química Orgánica General, CSIC
C/Juan de la Cierva 3, 28006 Madrid (Spain)

We show that $[\text{Cu}_3(\text{BTC})_2]$ and IRMOF-3-SI-Au are active and selective toward the cyclopropanation of alkenes without losing the crystalline nature of the MOF and hence can be reused without further modification. These MOFs are materials that can help to bridge the gap between homogeneous and heterogeneous catalysis.

Results and Discussion

Compounds $[\text{Cu}_3(\text{BTC})_2]$ and IRMOF-3-SI-Au were tested as heterogeneous catalysts for the cyclopropanation of alkenes due to the presence of well-defined, isolated, and stable copper(II) and gold(III) active sites that are fully accessible to the reactant.

The structure of $[\text{Cu}_3(\text{BTC})_2]$ consists of a cluster of two metal atoms that have a paddle-wheel shape and a square-planar coordination.^[11] The BTC ligand acts as a trigonal-planar ligand that connects the diatomic metal clusters,^[11b] which defines the nanocages. The $\{\text{CuBTC}\}$ structure comprises two types of “cage” and two types of “window” that separate these cages. Large cages are interconnected by 9 Å windows with a square cross-section. The large cages are also connected to tetrahedral-shaped pockets of approximately 6 Å through triangular-shaped windows of approximately 4.6 Å (Figure 1). At this point, we believe that the

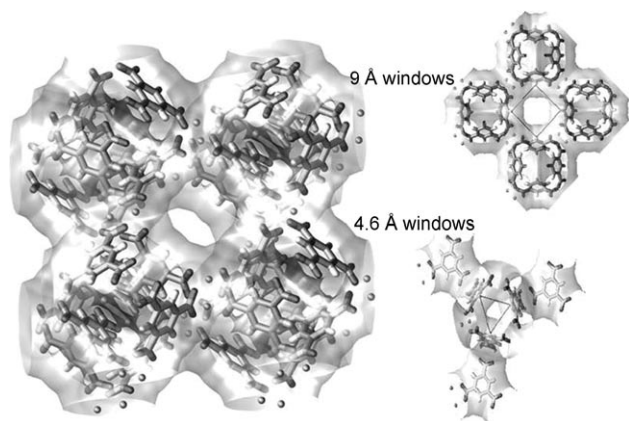


Figure 1. Crystal structure of the $[\text{Cu}_3(\text{BTC})_2]$ MOF.

activity of the catalyst may depend on 1) the availability of significant numbers of accessible sites due to the open MOF crystal structure, 2) the reversible coordination of organic linkers with the metal atom, and 3) the influence of the electrostatic field in the cavity by the partially charged framework. It has been previously reported that the active sites in $[\text{Cu}_3(\text{BTC})_2]$ are Lewis acids^[12] and IRMOF-3-SI-Au is an excellent catalyst for domino-coupling and cyclization reactions.^[5] We have now explored their activity as heterogeneous selective catalysts in the cyclopropanation of alkenes.

Catalysis with the copper-containing MOF: Initially, we focused on control experiments to optimize suitable conditions

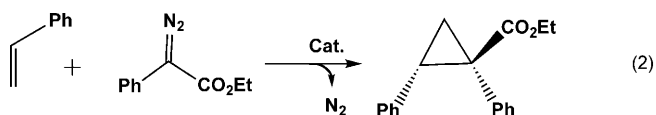
for an efficient and mild catalytic cyclopropanation reaction with ethyl diazoacetate (EDA) in the presence of $[\text{Cu}_3(\text{BTC})_2]$. In these initial studies, styrene was chosen as a model substrate. In our cyclopropanation experiments, the diazo compound was slowly added over two hours to the reaction mixture, which contained the catalyst and olefin, with a syringe pump. GC and GC–MS analyses of the reaction mixtures showed that cyclopropanes (as *cis/trans* mixtures) are formed as the main products of these reactions (50–90%) together with minor amounts of coupling products. $[\text{Cu}_3(\text{BTC})_2]$ -catalyzed transfer of a carbene unit from EDA to styrene was initially carried out in the absence of a solvent. Under these experimental conditions, the cyclopropanecarboxylates were obtained with low selectivity due to the formation of relatively large amounts of dimerization products, together with *ortho*, *meta*, and *para* aromatic addition products. The activity of the catalyst in this transformation can be estimated on the basis of the time required for the complete consumption of the alkene. Comparison with other copper catalysts, such as, the homogeneous catalyst^[13] Cu–H or copper complexes supported on ultrastable Y (USY) and MCM-41 matrices (Cu–USY, Cu–MCM-41), shows that $[\text{Cu}_3(\text{BTC})_2]$ displays similar rates but higher selectivities (Table 1).

Table 1. Catalytic results for the cyclopropanation reaction involving styrene and alkyl diazoacetates.

Entry	Catalyst ^[a]	Diazo Compound	Conversion [%] ^[b]	<i>t</i> [h]	Selectivity [%]	d.r. [%] ^[c]
1	$[\text{Cu}_3(\text{BTC})_2]$	EDA	98	3	98	71
2	Cu–H	EDA	74	2	49	59
3	Cu–USY	EDA	32	20	100	55
4	Cu–MCM-41	EDA	60	21	100	59
5	$[\text{Cu}_3(\text{BTC})_2]$	<i>t</i> BuDA	25	24	100	68
6	Cu–H	<i>t</i> BuDA	74	2	48	61
7	Cu–USY	<i>t</i> BuDA	23	19	100	62
8	Cu–MCM-41	<i>t</i> BuDA	57	19	100	59

[a] Catalyst loading: 5 mol %. [b] Selectivity towards cyclopropanes; the remaining diazo compound was converted into coupling products. [c] Diastereomeric selectivity: (*trans*–*cis*)/*trans* + *cis*.

The use of ethyl 2-phenyldiazoacetate (PhEDA) with $[\text{Cu}_3(\text{BTC})_2]$ as the catalyst in the cyclopropanation reaction of styrene provided better results [Eq. (2) and Table 2, entry 1]. A unique diastereoisomer (*trans*-Ph/COOEt) was obtained, similar to other systems reported for this substrate with this diazo compound.^[14] The reaction times required for complete diazo consumption are similar to those for EDA.



In a second series of experiments, β -methylstyrene was chosen as the substrate for the cyclopropanation reaction

Table 2. Cyclopropanation of alkenes with a $[\text{Cu}_3(\text{BTC})_2]$ -based catalyst^[a]

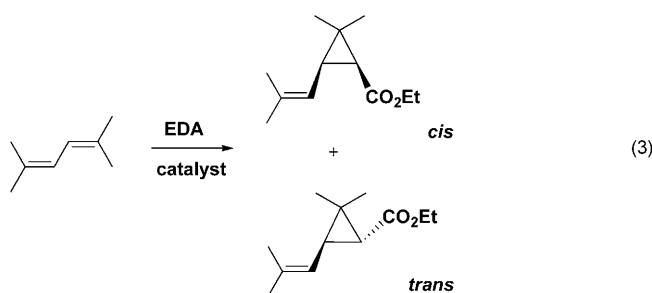
Entry	Olefin	Diazo compound	<i>t</i> [h]	Yield [%] ^[b]	d.r. [%] ^[c]	TON ^[d]
1	styrene	PhEDA	4	85	100	150
2	α -methylstyrene	PhEDA	4	50	100	70
3	β -methylstyrene	PhEDA	2	30	100	35
4	1-octene	PhEDA	3	90	98	165
5	cyclooctene	PhEDA	5	70	98	86
6	styrene	EDA	3	98	71	192
7	styrene	<i>t</i> BuDA	24	25	68	42
8	α -methylstyrene	EDA	2	25	58	48
9	α -methylstyrene	EDA	20	43	56	80
10	β -methylstyrene	EDA	15	50	67	100
11	DMHD	EDA	2	15	100	30
12	DMHD	EDA	20	60	100	120
13	1-octene	EDA	2	98	67	196
14	cyclohexene	EDA	2	99	98	196
15	cyclooctene	EDA	2	30	71	56
16	cyclooctene	EDA	2	30	57 ^[e]	60
17	dihydropyran	EDA	24	90	91	198

[a] Catalyst loading: 5 mol%. [b] Yield of the cyclopropane; the remaining diazo compound was converted into autocoupling products. [c] Diastereomeric selectivity: (*trans*–*cis*)/*trans* + *cis*. [d] Calculated as mmol of converted substrate/mmol of catalyst. [e] Experiments in which EDA was completely added before starting the reaction.

with the same copper catalyst and PhEDA as the carbene source. Again, only one cyclopropane stereoisomer was obtained. Substrates 1-octene and cyclooctene were treated with PhEDA, and the same high diastereoselectivities were obtained (Table 2, entries 4 and 5). The optimized protocol was extended to other substrates to determine the scope of the catalytic activity of $[\text{Cu}_3(\text{BTC})_2]$ and also to study the chemoselectivity and diastereoselectivity of the cyclopropanation (Table 2). We focused on three types of olefin: styrenes (styrene, α -methylstyrene, β -methylstyrene), linear alkenes (1-octene, 1-decene), cyclic olefins (cyclohexene, cyclooctene, dihydropyran), and 2,5-dimethyl-2,4-hexadiene (DMHD) with EDA, PhEDA, and *tert*-butyl diazoacetate (*t*BuDA) as the cyclopropanating agents (Table 2). To evaluate these MOF-catalyzed reactions, the reactivity of different styrene derivatives was studied. The presence of electron-withdrawing or -donating groups on styrene does not affect the selectivity of the resulting cyclopropanes. Styrene was converted almost completely into cyclopropanecarboxylates in high yields (Table 2, entries 6 and 7). Substrates α -methylstyrene and β -methylstyrene were successfully cyclopropanated into the corresponding products in good yields with 60–70% diastereoselectivity. The reaction rates, characterized by the turnover number (TON), were lower than those for styrene. Interestingly, the aliphatic and cyclic olefins (i.e., 1-octene, 1-decene, cyclohexene, dihydropyran, and *cis*-cyclooctene) yielded the corresponding cyclopropanes. For terminal aliphatic alkenes (i.e., 1-octene, 1-decene), diastereoselection occurred toward the *trans* cyclopropane. The yields were moderate for 1-decene, which was also observed in other cases with these olefins in which the reactivity is lower than for styrene. On the contrary, the copper-containing MOF exhibited a remarkable diastereose-

lectivity in the cyclopropanation of internal olefins. In the case of cyclohexene or dihydropyran, a 92:8 *trans/cis* ratio was achieved. Finally, low yields of the corresponding cyclopropanecarboxylates were achieved with *cis*-cyclooctene. This behavior could probably be ascribed to the higher steric hindrance of the internal double bond of the olefin with respect to the terminal double bond. As a result, in the substitution of the labile aqua molecule, the internal olefin coordinates in a preferred direction to the copper center.

Together with monoalkenes, dienes were employed as substrates for the copper-catalyzed cyclopropanation reactions. Indeed, 3-(1-isobutenyl)-2,2-dimethyl cyclopropanecarboxylic acid (chrysanthemic acid) is a key intermediate of pyrethroid insecticides,^[6,15] and the conversion of DMHD into the corresponding chrysanthemate esters by means of diazoacetates continuously represents a fundamental target in industrial applicable processes^[16] [Eq. (3)]. Therefore, alkenes containing alkyl groups instead of aryl substituents can model, to a certain extent, the behavior expected for the corresponding diene. Very few examples of high diastereoselection have been reported so far for olefins with no aryl substituents. Consistently with the behaviour observed for mono-olefins, when the copper-containing MOF was used to catalyze the conversion of conjugated diolefins into the corresponding cyclopropanes (Table 2, entries 11 and 12), the *trans* isomer was always the major product.



Recycling of the copper-containing MOF: Reusability experiments conducted with $[\text{Cu}_3(\text{BTC})_2]$ demonstrated that the copper-containing MOF is stable and no loss of either activity or selectivity was detected for the cyclopropanation of styrene. Table 3 shows that the conversions and yields of the *cis*- and *trans*-cyclopropanation products derived from styrene were maintained within three cycles. A comparison of X-ray diffraction patterns of $[\text{Cu}_3(\text{BTC})_2]$ before and after several reaction runs did not reveal any significant dif-

Table 3. Recycling experiments in the cyclopropanation of styrene with EDA catalyzed by $[\text{Cu}_3(\text{BTC})_2]$ in CH_2Cl_2 at room temperature

Run	Conversion [%]	<i>cis/trans</i>	Selectivity [%] ^[a]
1	100	30:70	94
2	95	29:71	95
3	98	25:75	96

[a] Selectivity toward cyclopropanecarboxylates.

ferences (Figure 2), so that the structural integrity of the material is basically preserved after the catalytic use.

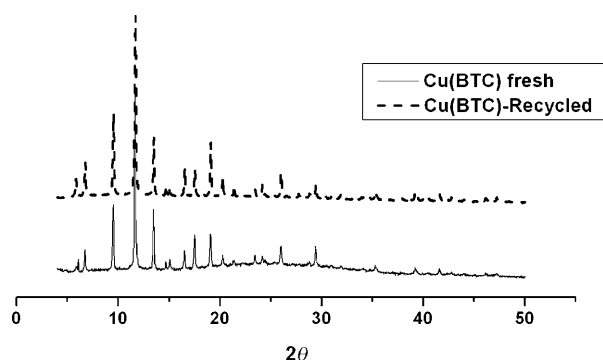


Figure 2. X-ray diffractograms of fresh $[\text{Cu}_3(\text{BTC})_2]$ and this MOF after several runs of the reaction.

The IR spectrum of fresh $[\text{Cu}_3(\text{BTC})_2]$ shows the characteristic carbonyl frequencies at $\tilde{\nu}=1630$ and 1645 cm^{-1} (Figure 3). A weak band in the carbonyl region at $\tilde{\nu}=$

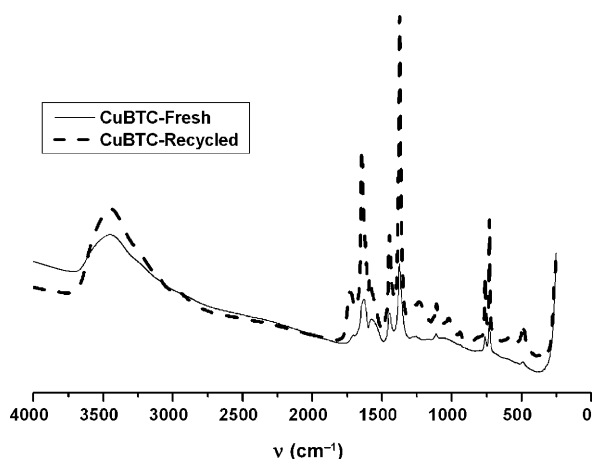


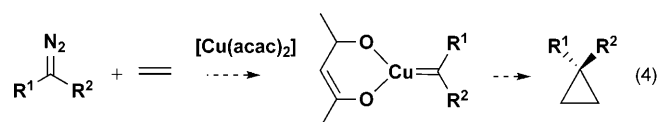
Figure 3. IR spectra before and after the reaction with $[\text{Cu}_3(\text{BTC})_2]$.

1705 cm^{-1} may point to a very small amount of free carboxylic groups, but the narrow and intense $\nu(\text{OH})$ band expected for an isolated benzenetricarboxylic acid is not observed, thus confirming that the amount of uncomplexed BTC in the solid is small.

The reusability of the material together with the fact that the metal loading (as determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES)) remained unchanged after the third cycle excludes the occurrence of metal leaching from the solid to the liquid. In a control experiment, the reaction was quenched after 15 min, the solid was filtered, and the copper content of the filtrate was analyzed to confirm the heterogeneity of the reaction. Inductively coupled plasma optical emission spectrometric (ICP-OES) analysis revealed that metal leaching was negligible. The reaction was continued with the filtrate but no further

conversion was observed. Thus, no dissolved active species are assumed to be present in reaction mixtures with the copper-containing MOF $[\text{Cu}_3(\text{BTC})_2]$ and the catalytic activity can be associated with the MOF structure.

Reaction mechanism: Although there are experimental studies on cyclopropanation through copper-catalyzed diazo decomposition, theoretical studies on Cu-carbene formation is rather scarce.^[17] In mechanistic studies on copper-catalyzed cyclopropanation reactions, the entire mechanism consists of steps that involve the formation of a copper-carbene moiety and the cyclopropanation reaction [Eq. (4); acac = acetylacetonate].



$[\text{Cu}_3(\text{BTC})_2]$ is a rigid MOF with a zeolites-like structure and free coordination sites on the copper(II) ion. The free coordination sites are oriented toward the center of one of the larger pores.^[18] The channel linings can be chemically functionalized and the aqua ligands can be replaced by other groups. For example, the treatment of the anhydrate $[\text{Cu}_2(\text{BTC})_3]_n$ with dry pyridine (py) gave $[\text{Cu}_2(\text{BTC})_3(\text{py})_3]_n \cdot 0.5\text{ py} \cdot 2\text{ H}_2\text{O}$, which gave an X-ray diffraction pattern similar to the original structure and therefore demonstrates that chemical functionalization can be achieved without a loss of structural integrity. During the cyclopropanation reaction, the aqua ligands can be replaced by the carbene unit and one carboxylate ligand can be replaced by the alkene, thus giving the corresponding metallacyclobutane. The IR spectrum of the copper-containing MOF recorded after reaction shows new bands at $\tilde{\nu}=1735\text{ cm}^{-1}$, which corresponds to the presence of new CO groups (Figure 3). The spectrum also shows new bands at $\tilde{\nu}=2985$, 2933 , and 2909 cm^{-1} , which can be assigned to the CH frequencies of the diazoacetate ester of a coordinated carbene unit. This intermediate formed by a four-centered pathway, involving favorable interactions between the copper center and the carbonyl group, appears to be the more facile route when the diazo compound has carbonyl group(s).

Catalysis with the gold-containing MOF: The preparative procedure for the synthesis of IRMOF-3-SI-Au has been reported elsewhere (Figure 4).^[5] We used the covalent post-synthetic methodology to prepare MOFs with open metal sites for potential use in catalysis. We prepared a MOF containing a gold(III)/Schiff base complex that lined the pore walls. The XRD pattern of IRMOF-3-SI-Au corresponds to a crystalline material with the expected structure. The absence of a diffraction peak at $2\theta=38.2^\circ$ (Au[111]) excludes the occurrence of metallic gold particles of $\geq 5.0\text{ nm}$.

It has recently been reported that the reaction of EDA with styrene does not proceed in the presence of cationic gold complexes.^[10b] In fact, after four days at room tempera-

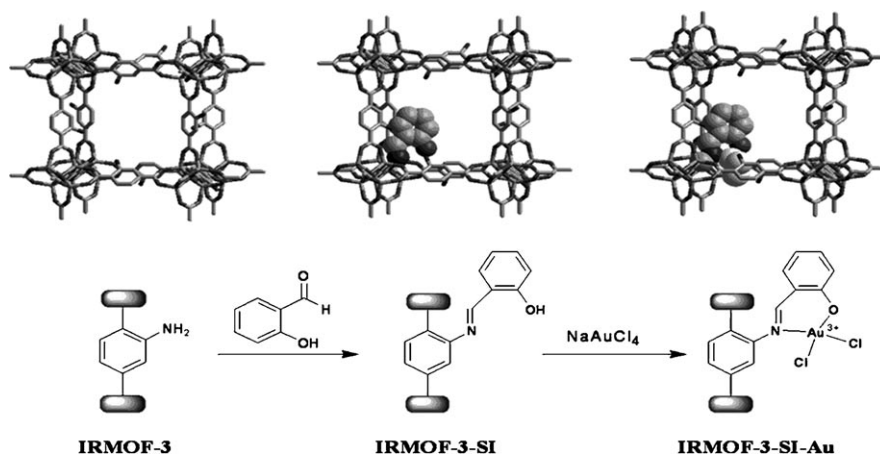


Figure 4. The postsynthetic modification procedure used to obtain MOFs containing gold(III)/Schiff base complexes.

ture the corresponding cyclopropane-containing product was not detected. However, when using our IRMOF-3-Si-Au solid catalyst at room temperature, conversions of up to 42% were obtained for the cyclopropanation of styrene with EDA (this MOF was also an active catalyst for the cyclopropanation of a variety of alkenes with EDA; Table 4). PhEDA produced better yields in the cyclopropanation of styrene (Table 4). It appears that gold-containing MOFs can also be an interesting solid catalyst for cyclopropanation reactions, although the activity is lower than for the copper-containing MOF.

Table 4. Cyclopropanation of alkenes with IRMOF-3-Si-Au^[a]

Entry	Alkene	Diazo compound	<i>t</i> [h]	Yield [%] ^[b]	d.r. [%] ^[c]	TON ^[d]
1	styrene	EDA	6	42	54	270
2	styrene	PhEDA	1	60	95	200
2	β -methylstyrene	EDA	15	40	59	240
3	DMHD	EDA	20	25	100	182
4	1-octene	EDA	22	45	56	170
5	cyclohexene	EDA	2	50	100	130

[a] Catalyst loading: 5 mol%. [b] Yield of cyclopropane; the remaining diazo compound was converted into coupling products. [c] Diastereomeric ratio: *trans/cis*. [d] Calculated as mmol of converted substrate mol⁻¹ of catalyst.

Recycling of the gold-containing MOF: Table 5 and Figures 5, 6, and 7 show the results of the recycling experiments with IRMOF-3-Si-Au. The IR and ¹³C magic-angle spinning (MAS) NMR spectra of the compound after the reaction

Table 5. Recycling experiments of cyclopropanation of 1-octene with EDA catalyzed by IRMOF-3-Si-Au in CH₂Cl₂ at room temperature

Run	Conversion [%] ^[a]	<i>cis/trans</i>	Selectivity [%] ^[b]
1	60	20:26	85
2	75	25:33	88
3	70	22:29	85
4	65	23:31	85

[a] Conversion after 24 h. [b] Selectivity toward cyclopropanecarboxylates.

are identical to the fresh catalyst. The IR spectra show the characteristic bands $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{C})$ at $\tilde{\nu}=1654$, 1600, and 1575 cm⁻¹ and the $\nu(\text{Au}-\text{O})$ band at the same position (before and after the reaction; i.e., $\tilde{\nu}=575$ cm⁻¹). The ¹³C NMR spectra present a resonance due to the C-O-Au unit at $\delta=167$ ppm. The structural integrity of the material is basically preserved after the catalytic use (Figure 5), although XRD studies indicate a small decrease in the crystallinity in the reused sample (Figure 7). The absence of the [111] peak of metallic gold on the reused

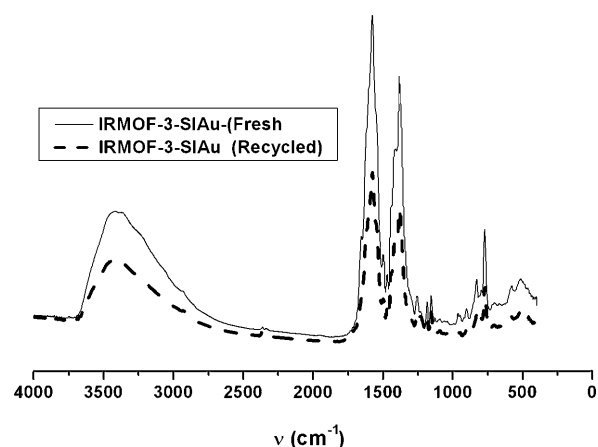


Figure 5. IR spectra of fresh IRMOF-3-Si-Au and this MOF recovered after three runs.

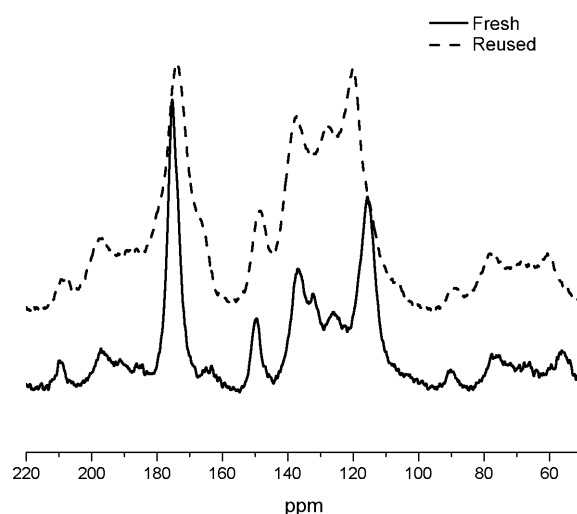


Figure 6. Solid-state ¹³C-MAS NMR spectra of fresh IRMOF-3-Si-Au and after several runs of the reaction.

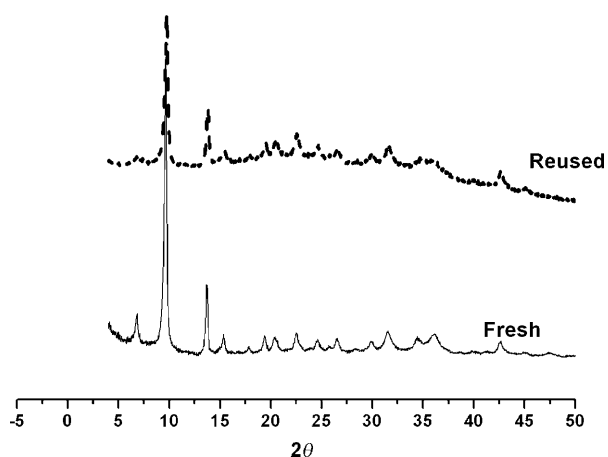


Figure 7. XRD pattern of the fresh and reused IRMOF-3-SI-Au catalyst.

catalyst shows that reduction of the gold(III) center does not occur during the reaction.

Conclusion

We have described the use of MOF materials that contain either copper or gold centers as catalysts for the cyclopropanation of alkenes with diazoacetates. This example is the first use of these materials to induce a carbene transfer reaction from diazo compounds. When using ethyl 2-phenyldiazoacetate, the copper catalyst showed very high chemo- and diastereoselectivities toward the *trans* isomer. Contrary to previously reported results that employed cationic gold complexes, the gold-containing MOF described herein is active and selective for the cyclopropanation of styrene with EDA. Nevertheless, its activity is lower than the copper-containing MOF. The conventional filtration test and recycling experiments demonstrate that the copper- and gold-containing MOFs are truly heterogeneous and reusable catalysts. The advantages of the present protocol include 1) cheap and reusable catalysts, 2) a simple workup and separation of the products from the reaction system that can be achieved by simple filtration, and 3) a highly selective catalytic system that performs better than other solid catalysts presented before. It appears that MOFs can establish a bridge between homogeneous and heterogeneous catalysts for cyclopropanation reactions.

Experimental Section

Materials and methods: All the preparations and manipulations were carried out in an oxygen-free nitrogen atmosphere using conventional Schlenk techniques. Metal contents were analyzed by atomic absorption with a Perkin-Elmer Analyst 300 atomic-absorption apparatus and plasma ICP Perkin-Elmer OPTIMA 2100 DV. The IR spectra were recorded on a Bruker IFS 66v/S spectrophotometer (range $\tilde{\nu}$ =4000–200 cm^{-1}) in KBr pellets. High-resolution ^{13}C MAS or CP/MAS NMR spectra of powdered samples, in some cases also with a Toss sequence to

eliminate the spinning side bands, were recorded on a Bruker MSL 400 spectrometer equipped with an FT unit at 100.63 MHz; pulse width: 6 μs , 90°; contact time: 2 ms; recycle delay: 5–10. The spinning frequency at the magic angle (54°44') was 4 KHz. The olefins, EDA, and *tert*-butyl diazoacetate (*t*BuDA) were purchased from Aldrich. Ethyl 2-phenyldiazoacetate (PhEDA) was prepared according to reported methods.^[19] $[\text{Cu}_3(\text{BTC})_2]$ (BasoliteC 300 produced by BASF; Figure 1) was supplied by Aldrich (BET=1500–2100 m^2/g). The detailed preparation and characterization of IRMOF-3-SI-Au has been reported previously (Figure 4).^[5]

General procedure for the cyclopropanation reactions: The diazo compound EDA, PhEDA, or *t*BuDA (11 mmol) was added to the catalyst $[\text{Cu}_3(\text{BTC})_2]$ (0.04 mmol) or IRMOF-3-SI-Au (0.0011 mmol) and olefin (8 mmol) dissolved in dichloromethane (5 mL) either in one portion before starting the reaction or slowly in a dropwise manner with a syringe pump over 2 h. Gas evolution was observed along with a smooth change in color. The resulting mixture was stirred at room temperature for 24 h. The reaction was monitored by gas chromatography on an HP5890 II GC-MS chromatograph, cross-linked methyl silicone column (SPB): 25 $\text{m} \times 0.2 \text{ mm} \times 0.33 \text{ mm}$; carrier gas: helium; $P=20$ p.s.i.; injector temperature: 230 °C; detector temperature: 250 °C; oven program for styrene: 70 °C (3 min), 15 °C min^{-1} to 200 °C (5 min); retention times: EDA 3.2 min, styrene 3.82 min, *n*-decane 5.47 min, diethyl maleate 7.84 min, diethyl fumarate 8.02 min, *cis*-cyclopropane 10.91 min, *trans*-cyclopropane 11.41 min. When the nitrogen evolution was finished, the volatiles were removed and the extract was purified by flash chromatography with ethyl acetate/hexane (1:9) as the eluent. For the filtration tests, an aliquot of the reaction suspension was withdrawn at a certain conversion at the reaction temperature, the catalyst was separated, and the supernatant was allowed to react further in a separate vial.

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