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Mesoporous Metal Oxide Encapsulated Gold Nanocatalysts: Enhanced Activity for Catalyst Application to Solvent-Free Aerobic **Oxidation of Hydrocarbons**

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Supporting Information



ABSTRACT: Here, we present a series of experimental studies to encapsulate ultrasmall gold nanoparticles into mesoporous metal oxide via an in situ self-assembly method. Notably, the 2.0Au@mZnO catalyst (~2.0 nm gold nanoparticles loading on mesoporous ZnO nanospheres) shows excellent catalytic activity for indane oxidation (120 °C, conversion 88.5%) and affords much high turnover frequencies (9521 h^{-1}). The catalytic activity of these gold-based catalysts was found to be correlated with the size of gold nanoparticles and the types of metal oxide supports. With a decrease in gold nanoparticle size, the catalytic conversion efficiency of indane oxidation increased. In addition, such catalysts possessed high thermal and chemical stability and could be reused more than 10 times without a remarkable loss of catalytic activity.

INTRODUCTION

Metal-catalyzed C-H activation reactions are strategies for achieving highly valuable and structurally complex products from cheap, simple, and readily available organic substrates.^{1–3} The selective oxidation of C-H bonds is a primary transformation in organic chemistry.²⁻⁶ In general, various oxidants, such as halides,⁷ tert-butyl hydroperoxide,⁸ hydrogen peroxide, 9,10 and O_2^2 or ozone, 11 have been used for oxidation of C-H reactions. There is no doubt that O_2 is one of the most universal and environmentally friendly oxidants among those oxidants. However, the high C-H bond dissociation energies of hydrocarbons make it is difficult for oxygen molecules to oxidize the C-H bonds of hydrocarbons. Therefore, the development of selective oxidation of C-H bonds with O₂ as oxidant is still the greatest challenge in this field.

During the past few decades, various metal-based catalysts (such palladium-based catalysis,¹² Au-Pd alloy catalysis^{13,14}) have been studied for aerobic oxidation. Among those materials, nanosized gold-based materials are considered as being the most promising for C-H activation reactions, due to their extraordinary catalytic activity and resistance to poisoning by chemical groups and oxygen.^{15–17} Haruta and co-workers reported that Au nanoparticles (Au NPs) with sizes in the range of 2-5 nm show unusually excellent catalytic activities.¹⁸ However, Au NPs tend to grow or aggregate into larger particles under high-temperature treatment, which is a critical issue in stabilizing ultrasmall Au NPs.¹⁹ In addition, as many important catalytic processes require high reaction temperatures, the poor thermal stability of gold-based catalysts obstructs their use in real-world catalysis; therefore, improving their thermal stability is also urgent.^{20–22}

Loading small Au NPs on oxide supports by an impregnation method to stabilize the size of metal particles has been the most commonly used method.²³⁻³¹ Among various oxide supports, mesoporous metal oxides have been found to be the most helpful promoters in the catalytic reactions, because of fast mass transfer and confinement effect for loading particles.^{32–36} Unfortunately, this simple loading of Au nanoparticles makes gold easily aggregate because of strong Brownian motion, leading to a serious decrease in catalytic activity.^{19,37} So far, there is an urgent need to find an efficient and simple approach to stabilize ultrasmall gold nanoparticles.

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Figure 1. TEM images of different sizes of Au NPs ($2.0 \pm 0.3 \text{ nm}$ (a), $2.5 \pm 0.3 \text{ nm}$ (b), $3.0 \pm 0.3 \text{ nm}$ (c)) and the corresponding UV/vis spectra (d). The insets in (a)–(c) in each image are the size distributions of Au NPs.

Scheme 1. Schematic Illustration of the Synthetic Procedure for Au NPs@mMO_x Nanospheres



In this work, we develop a series of high-performance heterogeneous catalysts by encapsulating ultrasmall Au NPs on mesoporous metal oxides via an in situ self-assembly method. The separated Au NPs were tightly anchored on the inner walls of the mesoporous metal oxides and were successfully stabilized by interface and space confinement effects. In comparison with the impregnation approach, the encapsulated Au NPs via the self-assembly method exhibited much higher activity and stability. In particular, the obtained 2.0Au@mZnO (2.0 nm Au NPs loaded on mesoporous ZnO) turned out to be highly active in the oxidation of indane (conversion 88.5%, TOF 9521) with molecular oxygen as the oxidant. Moreover, these catalysts present excellent thermal stability and can be subjected to long-term high-temperature treatment at temperatures up to 500 °C. In addition, we further investigate the effect of the gold nanoparticle size and the support species on catalytic activity.

EXPERIMENTAL SECTION

Au NPs were dispersed in 5 mL of chloroform with a concentration of 6.7 mg/mL. Then 0.1 mL of the gold solution in chloroform was added to 20 mL of CTAB aqueous solution (0.055 M) with vigorous stirring. Then the solution was aged at 60 $^{\circ}$ C for 10 min with stirring to remove the chloroform, giving a clear black Au@CTAB solution. The resulting mixture was mixed with a solution of 270 mL of water, 18 mL of 0.025 M ascorbic acid, 36 mL of 0.023 M CTAB, 36 mL of

0.023 M Zn(NO₃)₂ and 18 mL of a 0.047 M hexamethylenetetramine (HMT) solution. Then the mixture solution was reacted at 85 °C for 8 h. The as-synthesized products were separated by centrifugation at 10000 rpm. The obtained products were washed with ethanol and distilled water several times and then dried at 70 °C overnight. The as-synthesized samples were calcined in air at 300 °C for 2 h at a heating rate of 2 °C min⁻¹. The obtained samples with different gold sizes were denoted 2.0Au@mZnO, 2.5Au@mZnO, and 3.0Au@mZnO, respectively. 2.0Au@mCeO₂ and 2.0Au@mCuO catalysts were synthesized in the same way (cerium nitrate or copper nitrate was used as a precursor).

RESULTS AND DISCUSSION

In the first phase of our work, Au NPs with different sizes were synthesized according to the literature.^{38,39} Figure 1a–c shows transmission electron microscopy (TEM) images of the 2.0 nm (Figure 1a), 2.5 nm (Figure 1b), and 3.0 nm (Figure 1c) Au NPs synthesized in this work. UV/vis spectra of the Au NPs with different sizes dispersed in chloroform all exhibit the characteristic Au absorption between 520 and 530 nm (Figure 1d). Then Au NPs were assembled within mesoporous ZnO nanospheres by an in situ self-assembly method. The synthetic protocol is represented in Scheme 1. First, organic-ligand-protected Au NPs were encapsulated in the hydrophobic core of hexadecyl trimethylammonium bromide (CTAB) micelles. Then CTAB serves as a bridge for the in situ formation of



Figure 2. TEM images of 2.0Au@mZnO before calcination (a) and after calcination at 300 $^{\circ}$ C (b). Mapping and EDX of 2.0Au@mZnO after calcination at 300 $^{\circ}$ C (c, d). XRD patterns (e) and TG analysis in air (f) of 2.0Au@mZnO after calcination at 300 $^{\circ}$ C (0.3 wt % loading rate of Au NPs).



Figure 3. TEM images (a, b) and XRD patterns (c) of 2.0 Au@mZnO after calcination at 400 and 500 °C. N₂ adsorption-desorption isotherms (d) of a 2.0Au@mZnO sample after calcination at different temperatures (inset in (d) is the corresponding pore size distribution of samples; 0.3 wt % loading rate of Au NPs).

mesoporous ZnO around Au-CTAB. As shown in Figure 2a, a TEM image of the representative 2.0Au@mZnO reveals that the individual Au NPs are homogeneously distributed throughout the zinc oxide nanosphere. As we all know, thiolate ligands negatively affect the catalytic activity of gold due to a simple site-blocking effect of the ligands between the reactant molecules and active gold atoms.³⁷ In this study, the organic ligands and surfactant in the sample were removed by calcination at 300 °C in air. Figure 2b shows that the size of Au NPs has a slight range of 2.0-3.1 nm after removal of the ligands. Energy dispersive X-ray (EDX) and element mapping measurements of the 2.0Au@mZnO sample shows the coexistence of Au, Zn, and O signals throughout the nanospheres (Figure 2c,d). No characteristic peaks of gold were observed in the X-ray diffraction (XRD) patterns, which further confirmed that gold still maintains a small size (Figure 2e). Thermogravimetric analysis (TGA) in air performed on a calcined sample indicates that the organic molecules were burned completely (Figure 2f). These analyses clearly indicate that gold nanoparticles were successfully stabilized by the mesoporous ZnO nanospheres after removal of the protective organic group through thermal treatment.

Furthermore, a series of tests for the 2.0Au@mZnO sample after calcination at different temperatures were undertaken to verify the thermal stability. The TEM images directly indicate the evolution of 2.0Au@mZnO at different treatment temperatures (Figure 3a,b). As the calcination temperature increases from 300 to 500 °C in air, the loaded Au NPs still maintained a small size, which confirmed by the XRD patterns (Figure 3c), HRTEM images, and corresponding Au NPs size distributions (Figure S1). The slight pore expansion of zinc oxide nanospheres might be due in part to the channel collapse with the gradual growth of nanocrystals. On calcination of 2.0Au@mZnO nanospheres at 800 °C, the size of the gold nanoparticles increased to 10–15 nm (Figure S2a), and sharp gold diffraction peaks were observed in the corresponding XRD pattern (Figure S2b). Figure 3d and Figure S2c.d present the N₂ adsorption-desorption isotherms and corresponding pore size distribution curves for 2.0Au@mZnO nanospheres with different calcination temperatures. The isotherm of these samples shows a type IV curve with distinct capillary condensation steps, indicating the presence of uniform mesopores. At relatively low pressures (0.2-0.4) the adsorption curves of these samples exhibit an apparent capillary step, suggesting the presence of a pore size of about 2.2 nm. The isotherm has a hysteresis loop at a relative pressure of 0.5-0.8, which indicates the existence of larger mesopores (6.1 nm) as calculated by the Barrett-Joyner-Halenda (BJH) method. With an increase in the calcination temperature, the surface areas of samples calculated by the Brunauer-Emmett-Teller (BET) decreased gradually from 159 to 27 m² g⁻¹, and the corresponding pore volumes decreased from 0.6 to 0.083 cm³ g⁻¹.

In order to prove the broad applicability of this method, mesoporous ZnO nanospheres as support to load gold nanoparticles with the size of 2.5 and 3.0 nm have been successfully prepared (the corresponding TEM images are shown in Figure S3). The N₂ sorption isotherms of mZnO, 2.5Au@mZnO, and 3.0Au@mZnO samples shows the characteristic of type IV curves with similar capillary condensation steps (Figure S4). In addition, we also synthesized 2.0Au@mCeO₂ and 2.0Au@mCuO nanospheres by this method, and the corresponding TEM images are shown in Figure S5. The N₂ sorption isotherms of 2.0Au@mCeO₂ and 2.0Au@mCuO samples show type IV isotherms, suggesting the presence of mesopores (Figure S6). The surface areas of 2.0Au@mCeO₂, and 2.0Au@mCuO after calcination are 110 and 20 m² g⁻¹, respectively. Regrettably, the calcination temperature had a dramatic effect upon the surface areas of mesoporous CuO (decreased from 119 to 20 m² g⁻¹), which may affect the mass transfer rate during the catalytic process.

We chose solvent-free oxidation of indane as a model reaction to investigate the catalytic activity of 2.0Au@mZnO using molecular oxygen as an oxidant under atmospheric pressure. Catalytic performances of samples are given in Table 1. No products were obtained when the reaction was run for

Table 1. Oxidation of Indane Catalyzed by Gold-Based Catalysts⁴

		product (product selectivity (%)			
	catalyst	1- indanol	1- indanone	T (°C)	$\begin{array}{c} TOF \\ (h^{-1}) \end{array}$	conversion (%)
1				80		
2	mZnO			80		
3	2.0Au@ mZnO	63	31	80	453	6.2
4		76	21	100		5.7
5	mZnO	73	26	100		8.2
6	2.0Au@ mZnO	64	35	100	8582	62.6
7	2.0Au@ mZnO	10	60	120	9521	88.5
8 ^b	2.0Au@ mZnO			120		
9	2.5Au@ mZnO	66	32	120	7820	78.3
10	3.0Au@ mZnO	60	31	120	7574	67.8
11	2.0Au@ mCuO	17	64	120	4157	45.6
12	2.0Au@ mCeO2	9	56	120	6302	76.4

^{*a*}The accurate amount of substrate was calculated by weight. TOF = [reacted mol of substrate]/ [(total mol of metal) × (reaction time)]. The TOFs were measured after the first 2 h of reaction. Reaction conditions unless specified otherwise: indane 5 mL, catalyst 10 mg (all the catalyst after 300 °C calcined), O₂ 1 bar, reaction time 20 h. ^{*b*}Under a nitrogen atmosphere (0.3 wt % loading rate of Au NPs).

20 h at 80 °C without addition of any catalyst, giving evidence that the auto-oxidation of indane by O₂ cannot proceed spontaneously (entry 1, Table 1). When it was catalyzed by the mZnO sample alone, the oxidation reaction of indane at 80 °C also did not produce any product (entry 2, Table 1). On catalysis by 2.0Au@mZnO, 6.2% indane conversion was afforded, and the main product was 1-indanone (entry 3, Table 1). The above results show that 2.0Au@mZnO as a heterogeneous catalyst indeed promoted the air oxidation of indane. Notably, the conversion of indane was markedly improved to 62.6% in 20 h when the reaction temperature was increased to 100 °C (entry 6, Table 1). However, the blank (entry 4, Table 1) and pure mZnO (entry 5, Table 1) oxidationd only gave 5.7% and 8% indane conversion, respectively, at 100 °C due to noncatalytic oxidation. It is significant that the 2.0Au@mZnO catalyst reached a high indane conversion value of 88.5% when the reaction

temperature was increased further to 120 °C (entry 7, Table 1). This conversion value of indane is noticeably higher than that for other catalysts under the same reaction conditions (Table S1). All of these results suggested that the reaction temperature had a significant influence on indane oxidation. In addition, no product was obtained when the indane oxidation reaction was carried out under an N₂ atmosphere, indicating that O₂ is actually important in the reaction (entry 8, Table 1).

In order to study the surface chemical composition and the oxidation state of the catalysts, X-ray photoelectron spectroscopy (XPS) spectra for the Au 4f and O 1s core levels of the mZnO and 2.0Au@mZnO samples were recorded (Figure 4a–



Figure 4. XPS spectra of the O 1s peaks of mZnO (a) and 2.0Au@ mZnO (b). XPS spectra of the Au 4f peak of 2.0Au@mZnO (c) (0.3 wt % loading rate of Au NPs).Time-activity profile for the indane aerobic oxidations (d). Reaction conditions: indane 5 mL, 2.0Au@ mZnO 0.01 g, 100 °C, O₂ 10 mL min⁻¹, stirring speed 1000 rpm.

c). The XPS spectra of the Au $4f_{7/2}$ core levels consists of three bands, which can be assigned to Au^+ Au^{3+} , and $Au^{0.40}$ Meanwhile, the O 1s spectrum was fitted into three peaks at 529.4, 531.2, and 533.1 eV, respectively. The peak at 529.7 eV was ascribed to lattice oxygen atoms (O^{2-}) , the peak at 531.1 eV was ascribed to surface oxygen species (for example, O_2^- , O_2^{2-} , O⁻ "reactive" oxygen species), and the peak at 533.1 eV was ascribed to chemisorbed water or carbonates.³³ The concentration of "reactive" oxygen species atoms of the 2.0Au@mZnO sample was calculated by integrating the peak areas of different oxygen species. The results reveal that the atomic ratio of surface oxygen species in mZnO nanospheres increases from 30% to 69% after loading of 2.0 nm Au NPs. These results can be rationalized by assuming the existence of Au³⁺, Au⁺, and a large number of oxygen defect sites in the 2.0Au@mZnO sample due to electron transfer between Au NPs and mZnO nanospheres. According to the literature, the "reactive" oxygen species from defective sites have a great influence on the catalytic oxidation process. The high ratios of "reactive" oxygen species in ZnO might result in the exceptional catalytic activity of the 2.0Au@mZnO catalyst.

Figure 4d shows the variation of the product distribution detected by GC-MS. The $O_2^{\bullet-}$ superoxide which was generated from O_{22} forming collisional charge transfer

complexes with aromatic rings, can trigger some aerobic oxidation.⁴¹⁻⁴³ For indane oxidation, the rate of $O_2^{\bullet-}$ superoxide generation increased in the presence of 2.0Au@mZnO as catalyst. In this process, the organic hydroperoxides further decomposed into 1-indanol/1-indanone as the reaction time increased. On the basis of the 2.0Au@mZnO characterization and the temporal variation of the product distribution for indane oxidation, a reasonable mechanism for the catalytic reaction is described in Scheme 2.

Scheme 2. Proposed Reaction Pathway for the Oxidation of Indane Using 2.0Au@mZnO as Catalyst at 100 °C



Then, we investigated the effect of the size of gold nanoparticles on the catalytic performance of the Au@mZnO catalyst. The results show that the catalytic activity decreased in the order 2.0Au@mZnO > 2.5Au@mZnO > 3.0Au@mZnO; the conversion values of indane are 88.5% (2.0Au@mZnO), 78.3% (2.5Au@mZnO), and 67.8% (3.0Au@mZnO) (entries 7, 9, and 10, Table 1). The XPS spectra of the O 1s peaks of 2.5Au@mZnO and 3.0Au@mZnO are shown in Figure S7. The atomic ratios of "reactive" oxygen species in 2.5Au@mZnO and 3.0Au@mZnO were 64.5% and 43.1%, respectively. Overall, the calculation results suggested that with an increase in particle size the oxygen vacancies in the catalyst are decreased, which might be the reason 2.0Au@mZnO has the highest catalytic activity in this work.

In addition, we also studied the effect of supports on catalyst activity. The 2.0Au@mCuO and 2.0Au@mCeO2 catalysts also achieved remarkably high TOFs (4157 and 6302 h^{-1}) during the oxidation of Indane (entries 11 and 12, Table 1). The XPS spectra of the O 1s peaks of mCeO₂, 2.0Au@mCeO₂, mCuO, and 2.0Au@mCuO samples are shown in Figure S8. We found that the gold-support interactions resulted in a large number of oxygen defect sites in the metal oxide support. The interactions between gold and different types of supports lead to different concentrations of surface oxygen species in the support. The atomic ratio of "reactive" oxygen species in 2.0Au@mCeO2 and 2.0Au@mCuO catalysts are 59% and 30.4%, which are smaller than that in the 2.0Au@mZnO sample. Furthermore, the surface areas of 2.0Au@mCeO₂ and 2.0Au@mCuO are both lower than that of the 2.0Au@mZnO sample, which might lead to slower mass diffusion/transfer in the catalyst process. The concentrations of "reactive" oxygen species atoms and the surface areas of these catalysts are summarized in Table S2. The ratio of "reactive" oxygen species in catalyst to the surface areas of supports might affect the catalytic performance.



Figure 5. Reaction kinetics plots (a, c, d) and the Arrhenius plot (b) for the indane aerobic oxidations by gold-based catalysts with O_2 : (a, b) 2.0Au@mZnO 0.01 g; (c) 2.0Au@mCeO₂ 0.01 g; (d) 2.0Au@mCuO 0.01 g. Reaction conditions: indane 5 mL, 100 °C, stirring speed 1000 rpm. C_0 is the original concentration of the substrate and C_t the concentration of substrate at time t (0.3 wt % loading rate of Au NPs).

The rate constant k is shown in Figure 5a. The indane oxidation reaction with 2.0Au@mZnO as catalyst showed a relatively high k value of 0.014 \pm 0.061 h⁻¹. According to the Arrhenius equation $\ln k = -E_a/RT + \ln A$ (k, rate constant; E_a , apparent activation energy; A, pre-exponential factor), we plotted ln k versus 1/T, where k is calculated by linearly fitting the concentration curve of indane within the initial 300 min of reaction at an indicated temperature. The E_a value for the oxidation of indane is 35.5 kJ mol⁻¹, this extremely low value suggesting an easily initiated reaction (Figure 5b). When indane oxidations were catalyzed by both 2.0Au@mCeO₂ and 2.0Au@mCuO, k values of 0.02 ± 0.035 and 0.019 ± 0.056 h^{-1} , respectively, were obtained (Figure 5c,d). In general, the ability to reuse and recover the catalyst after the reaction is the best advantage of heterogeneous catalysis.² The 2.0Au@mZnO catalyst is very stable and can be reused more than 10 times without remarkable loss of activity for indane oxidation, and the corresponding conversion rate was estimated to be $\sim 60\%$ (Figure S9). Figure S10 shows the XRD pattern, TEM and SEM images, and N₂ adsorption/desorption isotherm of the 2.0Au@mZnO sample after catalysis cycling experiments. We can clearly observe that the sizes of the gold nanoparticles and the surface compositions of catalysts undergo no obvious changes. In consideration of these results, it is reasonable to confirm that the gold-based catalyst is indeed useful in practical heterogeneous catalysis.

Given these encouraging results, we also investigated some solvent-free oxidation reactions for other hydrocarbons to extend the application range of the 2.0Au@mZnO catalyst. Selective oxidation of tetralin to α -tetralol and α -tetralone is an important process in the synthetic commercial production of α -naphthol, pharmaceuticals, and agrochemicals (entry 1, Table 2).^{43,44} Diphenylmethane can be oxidized to diphenylmethanone with a moderate conversion of 12% in 20 h, possibly owing to a steric hindrance effect (entry 2, Table 2). The 2.0Au@mZnO catalyst also has great functionality in the

Table 2. Oxidation of Hydrocarbons Catalyzed by 2.0Au@ $mZnO^{a}$

	Substrate	Product (Selectivity %)	T (°C)	TOF (h ⁻¹)	Conversion (%)
1	\mathbb{C}		100	7,986	58
2	010	C ⁱ C ₉₉	140	5,693	12
3 ^b	ÓÒ	€ ¹ 1096	120	478	86
4 ^{<i>c</i>}	Ô	$\overset{\text{``}}{\bigcirc}_{62} \overset{\text{``}}{\bigcirc}_{36}$	110	16,452	92
5	Ċ	€ 21 € 45	130	5,975	52
6	0^		120	9,955	17

^{*a*}The accurate amount of substrate was calculated by weight. TOF = [reacted mol of substrate]/ [(total mol of metal) × (reaction time)]. The TOFs were measured after the first 2 h of reaction. Reaction conditions unless specified otherwise: substrate 5 mL, 2.0Au@mZnO 10 mg, O₂ 1 bar, reaction time 20 h. ^{*b*}Reaction conditions: substrate 5 mmol, CH₃CN 5 mL, 2.0Au@mZnO 10 mg, O₂ 10 bar. ^{*c*}Reaction conditions: substrate 5 mL, 2.0Au@mZnO 10 mg, O₂ 10 bar, reaction time 20 h (0.3 wt % loading rate of Au NPs).

oxidation reaction of the large molecule fluorene with high selectivity (entry 3, Table 2). For the oxidation of cyclohexene it afforded a high conversion (92%), with cyclohexen-1-one and 2-cyclohexen-1-ol as the main products (entry 4, Table 2).

o-Xylene was oxidized at 130 °C with 1 bar of O₂, giving a TOF of 5975 (entry 5, Table 2). The ethylbenzene conversion was somewhat lower, due to the high C–H bond dissociation energy (87 kcal mol⁻¹) (entry 6, Table 2). Briefly, it is reasonable for us to say that the 2.0Au@mZnO in this work is a very suitable catalyst for aerobic oxidation of hydrocarbons under mild conditions.

CONCLUSIONS

In summary, we successfully synthesized high-performance gold-based catalysts by an in situ self-assembly method. We found that the catalytic activity of gold-based catalysts and the atomic ratio of "reactive" oxygen species in the support increases as the gold nanoparticle size decreases. The interactions between gold and different types of supports lead to different concentrations of surface oxygen species in the support. In addition, during the catalytic reaction, our catalysts exhibit excellent thermal stability and can be subjected to long-term high-temperature treatment at temperatures up to 500 °C. All of these results indicate that Au NPs@mMO_x nanospheres are ideal environmental catalysts for industrial applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b02197.

HRTEM and TEM images, N_2 adsorption-desorption isotherms, XPS spectra of O 1s peaks and XRD patterns of 2.0Au@mZnO, 2.5Au@mZnO, 3.0Au@mZnO, 2.0Au@mCeO₂, and 2.0Au@mCuO samples, recycling runs for the indane aerobic oxidations, concentrations of oxygen species atoms and surface areas of all catalysts, and indane oxidation catalytic activity with other reported catalysts (PDF)

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Notes

The authors declare no competing financial interest.

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