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C–X (X = Cl, Br, I) bond dissociation energy as a descriptor for the redispersion of sintered Au/AC catalysts

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ABSTRACT

Disintegration or redispersion of supported sintered gold nanoparticles (Au NPs) in the presence of alkyl halide can give catalyst regeneration or redispersion of sintered Au catalysts. The selectivity of alkyl halides, temperature and size distributions were investigated to elucidate the redispersion of Au NPs during halide-induced decomposition. This study proved that the alkyl halide induced the redispersion of sintered Au NPs which depended on the R–X (X = I, Br, Cl) bond dissociation energy (BDE) and thus provided a simple descriptor for the regeneration of inactive supported Au catalysts. A correlation between the BDE of R–X and dispersion efficiency was established. The tendency for disintegration and redispersion followed the R–X BDE of the alkyl halide. Compared to alkyl chlorides and bromides, iodides were more efficient for redispersing sintered Au NPs. As a descriptor, the BDE of R–I played a crucial role in particle redispersion. These findings provided insights into the mechanism of organic halide-induced Au NP disintegration and the effect of the halide type on the redispersion of sintered catalysts.

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1. Introduction

Supported Au catalysts have been widely studied in the last three decades because of their outstanding catalytic performance for a wide range of catalysis processes. The Haruta group [1] and Hutchings group [2] initially developed Au-based systems for low temperature CO oxidation and acetylene hydrochlorination over active Au-based catalysts. Thereafter, Au was shown effective for environmental protection [3], chemical production [4], energy catalysis [5], and catalytic applications [6].

The transformation of Au from an inert metal to a catalytically active material is due to the production of small NPs. The nature of the interaction with the support is important for the

activity and selectivity. Although highly dispersed Au particles possess outstanding selectivity in many cases, Au-based catalysts have a tendency to have low stability because of irreversible deactivation caused by sintering, which is an important factor in deactivation [7,8]. Two mechanistic models have been proposed for Au sintering: coalescence of small particles and Ostwald ripening for the growth of larger particles at the expense of smaller ones. They both result in the loss of active surface area [9,10]. Despite the fact that particle sintering is a common event leading to the deactivation of Au NP catalysts, there is a paucity of investigation on the regeneration of smaller, catalytically active Au NPs from the large particles formed after elevated temperature treatment and/or a reduction atmosphere [10–12]. To increase the lifetime of industrial cata-

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lysts, researchers must elucidate how to suppress particle sintering rate or redisperse the deactivated catalysts in a facile approach. Hence, methods for the redispersion of Au from large to small NPs would be a major application in the reactivation of Au catalysts to make these materials more likely to become viable and practical industrial catalysts. Many groups have conducted studies to minimize or reverse catalyst deactivation through sintering. The majority of the research in this field has been confined to supported metal catalysts [7,13,14]. Catalysts can be regenerated using CO and NO or iodomethane [7,14]. Moreover, an offline treatment is an effective regeneration method [15,16].

For heterogeneous catalysis, large Au NPs (~30 nm) are dispersed to form stable Au dimers and trimers during Au-catalyzed carbonylation of methanol to methyl acetate and ethanol dehydrogenation in the presence of iodomethane [7,15]. Sa' et al. [7] investigated the dispersion of Au NPs supported on activated carbon (Au/AC) and graphite by using a CH_3I treatment. The atomic dispersion of Au was achieved at a temperature as low as 50 °C. The proposed reaction mechanism suggested that Au was initially oxidized by interaction with iodine. This was followed by the dissociation of Au–I entities from the central particle. Furthermore, titania- and alumina-based supported Au catalysts were transformed from nm particles into small clusters and some atomically dispersed Au. Similarly, large particles of Au (12–28 nm in size) supported on activated carbon can be dispersed down to the atomic level during the carbonylation of methanol to methyl acetate in the presence of methyl iodide, which was reported by Goguet et al. [12]. The interaction of Au with iodine is important. Moreover, Morgan et al. [17] reported that Au dispersion was achievable under milder conditions in terms of temperature and pressure by using a simple CH_3X /inert feed ($\text{X} = \text{Br}$ or I). The markedly benign conditions were used to disperse the Au catalyst and, in this case, redispersed Au-supported carbon which were sintered to reactivate the catalyst [17]. Although this is a significant transformation, the conditions utilized during the reaction were harsh (240 °C and 1.6 MPa) and required a complex reaction mixture involving virulent reagents and security concerns. Furthermore the mechanism of redispersion by the organic halides remains ambiguous, thereby limiting the general applicability of the approach as a routine procedure for the dispersion of sintered Au catalysts.

Recently, we conducted a series of redispersion processes of sintered Au/AC catalysts using iodohydrocarbons, and indicated the correlation of the C–I BDEs of iodohydrocarbon and the redispersion rate where the minimum BDE exhibited the best redispersion efficiency [18]. Many studies used *in situ* high resolution transmission electron microscope (HRTEM) to evaluate direct sintering, Ostwald ripening, or aggregation of metal NPs, including Au [16,19,20]. Nevertheless, the readily visible disintegration or redispersion and formation of nanoclusters of sintered NPs were defective, especially Au NPs [21,22]. We previously proposed a mechanism that gave a molecular level understanding of the critical interfacial events and revealed the strategy of small Au NPs/cluster formation stability [18]. Halide ions were adsorbed on the Au surface with

binding energies that scale with polarizability ($\text{I}^- > \text{Br}^- > \text{Cl}^-$) and crystal facet $\{(111) > (110) > (100)\}$ [23,24]. To evaluate the Au dispersion efficiency, we showed that Au dispersion was alkyl halide-induced and well correlated with the R–X ($\text{X} = \text{I}, \text{Br}, \text{Cl}$) BDEs. The redispersion of already sintered Au/AC catalyst was easily achieved under mild and safe conditions in terms of temperature and type of alkyl halide. HRTEM images illustrated a direct redispersion progress. As a regeneration showcase, a hydrochlorination catalytic test was performed to examine the viability of the regeneration protocol by using an unpromoted Au/AC catalyst, which was significantly sintered to large Au NPs under practical conditions [25–27]. The mechanism underlying the redispersion was proposed.

To reveal the intrinsic effects and nature of the carbon-halogen bond on the redispersion of sintered Au/AC catalysts, we compared the redispersion rate using three series of halohydrocarbons, namely, iodohydrocarbons, bromohydrocarbons, and chlorohydrocarbons. In this study, we focus on the redispersion of sintered Au particles with controllable size by using halohydrocarbons. The specific redispersion procedure of a sintered Au/AC catalyst was monitored using time dependent X-ray diffraction (XRD) patterns and TEM images. On the basis of the analysis of the C–X ($\text{X} = \text{I}, \text{Br}, \text{Cl}$) BDEs, the correlation between the C–X ($\text{X} = \text{I}, \text{Br}, \text{Cl}$) BDEs of the halohydrocarbons and the relative redispersion rate was successfully established. This gave a descriptor to predict the redispersion behavior. A catalytic test using acetylene hydrochlorination was performed to demonstrate the efficiency of the redispersion. A redispersion mechanism was discussed.

2. Experimental

2.1. Materials

Commercially available reagents (such as the metal precursor $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ from Aladdin Chemistry Co., Ltd, assay: 49.7%) were used without purification unless specified. AR-grade iodohydrocarbons, including triiodomethane (CHI_3), iodomethane (CH_3I), *n*-iodopropane ($n\text{-C}_3\text{H}_7\text{I}$), *n*-iodobutane ($n\text{-C}_4\text{H}_9\text{I}$), iodobenzene ($\text{C}_6\text{H}_5\text{I}$), and *n*-iodopentane ($n\text{-C}_5\text{H}_{11}\text{I}$); bromohydrocarbons consisting of *n*-bromopropane ($n\text{-C}_3\text{H}_7\text{Br}$), bromomethane (CH_3Br), dibromomethane (CH_2Br_2), bromoform (CHBr_3), tetrabromomethane (CBr_4), and chlorohydrocarbons consisting of *n*-chloropropane ($n\text{-C}_3\text{H}_7\text{Cl}$), chloromethane (CH_3Cl), dichloromethane (CH_2Cl_2), chloroform (CHCl_3), and tetrachloromethane (CCl_4) were obtained from Aladdin and used without further purification. Distilled deionized water, hexane, ethanol, and acetone (AR grade) were used as indicated. Nitrogen, hydrogen chloride, and acetylene (99.999% purity) were purchased from Linde AG.

2.2. Catalyst preparation and redispersion procedure

Au/AC (1.0 wt% Au loading) catalysts were prepared by an incipient wetness impregnation technique previously described [18]. The carbon (40–60 mesh) was first washed with diluted aqueous HNO_3 (2.0 mol L^{-1}) solution at 80 °C for 5 h to

remove Na, Fe, and Cu. The carbon was filtered and washed with distilled water and dried at 150 °C for 12 h. The required amount of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ solution in aqua regia (6.3 mL) was dropped into the acid-washed carbon (40–60 mesh, 5 g) while stirring. The product was then dried at 110 °C for 12 h and used as the fresh catalyst. Various aging protocols were employed for the supported noble metal catalysts. Selection was conducted to facilitate detection analyses and emphasize the chemical features attributed to the sintering of the aged samples. Thus, the physical or chemical properties of the samples were clearly given when describing the characterization technique used. The fresh catalyst was hydrothermally aged for 5 h at 350 °C in a tubular oven in a flow of dry N_2 (40 mL min^{-1}) with a heating ramp of 10 °C min^{-1} . The aged catalyst was then obtained and designated as Au/AC. Redispersion treatment of sintered catalysts was carried out in a sealed glass vial. In a classic treatment, 4 mL iodohydrocarbon-acetone solution (30 wt%) was first mixed in a sealed sample vial and 200 mg of the sintered catalyst was added to the mixed solution. The sample was vigorously stirred with a magnetic stirrer at a designated temperature under ambient pressure for a fixed time. After treatment, the sample was filtered, washed with hexane, and dried at 110 °C for 12 h. The dried sample was then stored in a sealed sample vial.

2.3. Catalyst characterization

XRD patterns of the catalysts were recorded using a PANalytical X'pert Pro Super X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418$ nm) and a scanning angle (2θ) range of 10° to 90°. The tube voltage and current were 40 kV and 30 mA, respectively. Au crystallite size was calculated using the Scherrer equation, with the full width at half-maximum (FWHM) of the Au (111) diffraction peak at $2\theta = 38.4^\circ$. TEM images were obtained using a TECNAI F30 transmission electron microscope operated at an acceleration voltage of 300 kV. The selected area electron diffraction (SAED) pattern was recorded by aligning the electron beam perpendicular to one of the square faces of an individual Au NPs. The catalyst powder was ultrasonically dispersed in ethanol at room temperature for 30 min to prepare an appropriate sample for TEM observation. The dispersed sample was transferred onto a carbon-coated copper or molybdenum grid by dipping. The particle size distribution was evaluated based on measurements from the full TEM images. The actual Au content of the sample was analyzed by X-ray fluorescence (XRF) spectrometry using a PANalytical AXIOS PW4400 sequential spectrophotometer with a Rh tube as radiation source. Measurements were performed with pressed pellets containing 6 wt% wax. Characterization was also conducted by X-ray photoelectron spectroscopy (XPS) using a Quantum 2000 Scanning ESCA Microprobe instrument (Physical Electronics) equipped with an Al $\text{K}\alpha$ X-ray radiation source ($h\nu = 1486.6$ eV). The activated catalyst was collected and sealed under Ar atmosphere. The collected sample was compressed into a thin disk in a glove box and then transferred to the XPS apparatus analysis chamber. Binding energies were calibrated using the Si 2p peak at 103.7 eV as reference. Ex-

perimental errors were within ± 0.2 eV. Diffuse reflectance ultraviolet-visible (UV-vis) spectroscopy measurements were performed in a Lambda 650S UV-vis spectrophotometer equipped with a Harrick high temperature reaction chamber and an integrating sphere detector.

2.4. Catalytic activity test

The catalytic performance of acetylene hydrochlorination was evaluated in a fixed bed glass microreactor (i.d. of 8 mm) at 0.1 MPa [18]. The temperature of the reactor was regulated using a CKW 1100 temperature controller. The reactor was purged with nitrogen for 12 h before the reaction to remove water and air in the system. Hydrogen chloride gas was passed through the reactor at a flow rate of 20 mL min^{-1} to activate the catalyst. After the reactor was heated to 180 °C, hydrogen chloride (5.5 mL min^{-1}) was fed through the heated reactor containing 0.5 mL of the catalyst at a gas hourly space velocity (GHSV) of C_2H_2 at 600 h^{-1} . The reaction products were analyzed using an online gas chromatograph (GC-2060). Product distribution was determined under the following conditions: chromatographic column, type 2 m $\times$ ϕ 4 mm; coating, GDX-301; column temperature, 120 °C; FID detector; and detector and vaporizer temperature, 150 °C. Given that the individual substance had a high boiling point and low content, the products of acetylene hydrochlorination were quantified by the peak area normalization method. The conversion of acetylene (X_A) and the selectivity to V_{CM} (S_{VC}) were used to determine the catalytic performance. As hydrogen chloride was absorbed after the reaction, the volume of the reaction system was set to constant throughout the calculation. With the total volume regarded as a volume unit, X_A and S_{VC} were calculated as follows:

$$X_A = (1 - \varphi_{A1}) \times 100\% \quad (1)$$

$$S_{\text{VC}} = \varphi_{\text{VC}} / (1 - \varphi_{A1}) \times 100\% \quad (2)$$

where φ_{A1} was the volume fraction of the remaining acetylene and φ_{VC} was the volume fraction of vinyl chloride. To distinguish the catalytic performance, we employed a GHSV of C_2H_2 as high as 600 h^{-1} , which was higher than the velocity used for the evaluation of conventional HgCl_2 catalysts.

2.5. Bond energy analysis

Fundamental concepts in organic chemistry involve intrinsic relationships and consist of energetics, structure, and reactivity. The experimental and theoretical values for the BDEs are essential for chemical kinetics, free radical chemistry, and organic thermochemistry. Nevertheless, getting reliable data of the BDEs or internal chemical bond strength can be complex and trying [28,29].

The BDE for homolysis of the R–X bond is defined as the enthalpy change in the following fission:

Hence, BDE is also called the bond dissociation enthalpy. The species R–X can be molecules, radicals, ions, complexes, and clusters. BDEs are commonly referred to as bond strengths, binding energies, bond energies, and bond disruption energies (enthalpies). A variety of methods are available for determining

BDE values. The experimental BDE values of many important compounds have been measured by researchers worldwide. However, the BDE values remain controversial among scientists because a tedious work of experimental studies is involved to get the relative BDE values [29,30]. Although we collected the experimental data, including all the information is difficult because most users were concerned with reliable experimental values only [18,29,30].

As the descriptor of redispersion efficiency, the redispersion rate $\Delta\tau$ was used in the following equation:

$$\Delta\tau = (R_s - R_d)/\Delta t \quad (4)$$

where Δt is the treatment time of contact with iodohydrocarbons.

3. Results and discussion

To illustrate the redispersion behavior, we modeled Au NPs as spherical drops [31]. The R_s and R_d represent curvature radius of sintered and redispersed Au NPs, respectively (Fig. 1). As a main technique, powder XRD is widely employed in nanoscience investigation. The average size of Au NPs can be estimated from the full width at half maximum (FWHM) of the diffraction line by the Scherrer formula. Particle sizes below 3–4 nm in diameter were estimated from the TEM or HRTEM images. The XRD results reveal that the diameter of the Au particles was 1.6 nm and larger than 33 nm on the as-prepared and sintered Au/AC catalysts, respectively (Fig. 2), which was in good agreement with reported results [17,18]. The diffraction lines of the Au (111), (200), (220), and (311) displayed lattice planes and a monocrystal feature (Fig. 2). Apart from those associated with the carbon support, no other peaks were observed. A series of iodohydrocarbons were used to redisperse the sintered Au catalyst. When the sintered Au/AC catalyst was treated with triiodomethane (CHI_3 , commonly used as a wound disinfectant and has a lower toxicity than the other organic iodides) at 40 °C for 30 min, the diffraction lines of Au NPs almost disappeared (Fig. 2), indicating that the diameter of the Au was below 3 nm. The sintered Au NPs were then redispersed after CHI_3 treatment at 40 °C for different times (Fig. 1). Moreover, as a systematic investigation of iodohydrocarbons on the redispersion process of Au NPs, we previously showed that after treatment with iodopentane ($\text{C}_5\text{H}_{11}\text{I}$), the intensities of the Au diffraction patterns significantly decreased. When a similar treatment was carried out using iodobenzene ($\text{C}_6\text{H}_5\text{I}$), CH_3I , and iodopropane ($\text{C}_3\text{H}_7\text{I}$), the XRD patterns of Au NPs remained but their intensities decreased. The results indicated the reduction of intensities follow the order of C–I BDEs variation: $\text{C–I}_{\text{CHI}_3} < \text{C–I}_{\text{C}_5\text{H}_{11}\text{I}} < \text{C–I}_{\text{C}_3\text{H}_7\text{I}} < \text{C–I}_{\text{CH}_3\text{I}} < \text{C–I}_{\text{C}_6\text{H}_5\text{I}}$ [29]. The size decrease performance could be due to the varied BDEs of the C–I bond in the iodohydrocarbons employed: low BDEs

Fig. 2. XRD patterns of the sintered Au/AC catalysts before and after treatment with CHI_3 at 40 °C as a function of time.

resulted in small Au NPs. Furthermore, iodic species participated in the redispersion of sintered Au NPs [18,32].

The redispersion process is illustrated in the TEM image of the sintered catalyst treated with CHI_3 for 30 min. In this case, small particles were formed on the carbon carrier from large Au NPs with a mean size of 2.58 nm. The TEM images indicate that the average particle size of the sintered Au/AC decreased from 33 to 2.58 nm after the catalyst was treated with CHI_3 for 30 min. The average particle size decreased with increasing treatment time (Fig. 1 and Table 1). Au NPs were further decreased in size to 0.8 nm after treatment for 60 min (Fig. 3(e)). The corresponding HAADF-STEM images confirm the transformation of the NPs (Fig. 3(f)). This phenomenon reflected the characteristics of reverse agglomeration. Hence, the dispersion of Au NPs underwent dissociation as a function of time and was probably not terminated because of the high potential energy of the particles. In all probability, the disintegration of large particles suggests the spontaneous formation of a monolayer of iodine atoms on the Au surface after treatment with CHI_3 .

Table 1

Changes in the Au content analyzed by XRF and mean size of Au NPs estimated by XRD/TEM of the sintered Au/AC catalyst treated with CHI_3 at 40 °C as a function of time.

Time (min)	Au (wt%)	Time (min)	Mean size (nm)
0	0.94	0	33.2
30	0.72	5	11.2
60	0.79	10	8.2
120	0.82	15	5.1
180	0.81	30	2.6
300	0.82	60	0.8

Fig. 1. Schematic of the redispersion of supported Au NPs in a spherical model with radius R_s (sintered Au NPs) and R_r (dispersed Au NPs) of curvature.

Fig. 3. Representative TEM and HRTEM images of randomly selected areas in Au/AC catalysts. (a) Sintered catalyst, and the inset shows the selected area electron diffraction (SAED) pattern; (b–d) Sintered catalyst after treatment with CHI_3 , CHBr_3 , and CHCl_3 at 40 °C for 30 min, 12 h, and 12 h, respectively; the inset shows the selected area (red rectangle) that represents the lattice spacing of the Au(111) plane; (e, f) Typical HRTEM and DF-STEM images, respectively, of different randomly selected areas of the Au/AC catalyst images of sintered Au/AC after treatment with CHI_3 at 40 °C for 60 min.

[18,24]. These Au NPs underwent fusion and fragmentation on the support, since Au donates electrons to iodine atoms [24]. Furthermore, iodine adsorption on the NPs decreased the surface potential of Au NPs, resulting in enhanced driving forces [10]. Iodine-coated Au NPs also induced redispersion in a controlled manner on the carbon support. The activated carbon support was superior to other supports, such as SiO_2 and Al_2O_3 , in terms of capturing migrated Au NPs [24,33]. The combination with the redispersion process with C–I BDEs and the difference in size distribution with the different C–I BDEs could be due to the balance between the adsorption of iodic species and the surface potential energy of Au NPs. Iodoalkanes may function as a subsurfactant for size control [34,35]. Long-term redispersion confirmed the formation and controllable size of Au NPs/nanoclusters on the carbon support in a stable state [7].

The interaction among iodic species, Au atoms, and carbon carriers was determined using XPS data. Upon reaction with

different iodic compounds, the stability of the Au NPs in the final state may partially control the variation in particle size. The bond strength of $\text{CHI}_2\text{–I}$ is lower than that of $\text{C}_6\text{H}_5\text{–I}$ (203 vs. 272 kJ mol^{−1}), which may lead to the formation of small particles [36]. Changes in the C–I bond strength could be beneficial because a lower C–I BDE can be easily dissociated. Based on the analysis of BDEs, iodoalkanes with low BDE_{C–I} values produce high concentrations of iodic species in the liquid phase [7,37]. The dissociated iodic species reacted with Au NPs on the carbon support and induced the redispersion process. XPS data confirmed this (Fig. 4). The elemental concentrations and oxidative states of Au^0 , Au^{3+} and Au^+ on the Au/AC surface are summarized in Table 2. All evaluated catalysts exhibit Au^0 and Au^+ species, whereas the Au^{3+} species was present in the as-prepared catalyst only. Sintered Au/AC contained the highest amount of Au^0 species. When the sintered Au/AC was treated with CHI_3 at 40 °C for 60 min, the Au^+ content increased from 28.5% to 68.2%, which showed that Au^0 species were oxidized to Au^+ in the presence of CHI_3 [12]. Moreover, the binding energies of 619.1 and 620.9 eV could be attributed to I^- and polyiodic species (I_n^{m-} , $n \geq 1$, $0 \leq m \leq 1$), respectively (Fig. 4(c)). The I 3d XPS profile revealed the formation of auric iodide (Au_xI_y) [23,32]. With increasing treatment time, the Au content decreased from 0.94 to 0.72 wt% and gradually became constant at 0.8 wt% (Table 1). This result suggested that Au NPs were corroded and redispersed on the catalyst surface during the CHI_3 treatment. This protocol can be a potential alternative for the preparation of highly uniform and dispersed Au NP/nanocluster catalysts. Moreover, the diffusion of Au NPs after nucleation may involve a galvanic-reaction-like process, in which Au is reduced on Au nuclei through the transfer of electrons from the carbon surface, with the accompanying oxidation of the carbon support [38]. Considering the weak interaction between the carbon support and Au NPs, the C 1s XPS spectra of Au/AC catalysts showed negligible changes before and after Au sintering, as well as before and after redispersion with iodoalkanes (Fig. 4(d)).

To reveal the general relationship of BDEs and redispersion rate of the Au NPs to predict the redispersion efficiency, we need a descriptor for the prediction of the redispersion behavior. Halide ions are adsorbed on Au surfaces with binding energies that scale with polarizability ($\text{I}^- > \text{Br}^- > \text{Cl}^-$), resulting in different crystal facets $\{(111) > (110) > (100)\}$ [23,24]. To accurately evaluate the Au dispersion efficiency, we carried out Au dispersion by similar methods using another two series of alkyl halides, namely, bromohydrocarbons, and chlorohydrocarbons. The XRD patterns of the sintered Au catalyst samples treated with different bromohydrocarbons at 40 °C for 12 h are listed in Fig. 5(a). Compared with the treatment with iodoalkanes, the bromohydrocarbon treatment resulted in the incomplete vanishing of the Au features in terms of $\text{C}_3\text{H}_7\text{Br}$, CH_2Br_2 , and CHBr_3 with some features remaining, although with less intensity of the peaks upon CBr_4 treatment. In the case of the treatment with $\text{C}_3\text{H}_7\text{Br}$, minimal changes were observed in the XRD pattern because the treatment time and temperature affect redispersion. Evidently, prolonging the treatment time can induce high redispersion levels (Fig. 1),

Fig. 4. Au 4f XPS spectra of the sintered Au/AC catalysts (a) and sintered Au/AC treated with CHI_3 at 40 °C for 60 min (b); (c) I 3d XPS spectra of the redispersed Au/AC catalyst with CHI_3 at 40 °C for 60 min (sample (b)); (d) C 1s XPS spectra of carbon host (1) and Au/AC catalysts before (2) and after (3) redispersion with CHI_3 at 40 °C for 60 min.

indicating that variation in the size of Au NPs becomes arranged in the order from larger than 30 to 0.76 nm with the extension of treatment time [17,39]. The treatment temperature also significantly affected redispersion, as evidenced by the FWHM of the diffraction line and average size of Au NPs and the redispersion by treatment with CH_2Br_2 and diameter size distribution. High temperatures induced the formation of small Au NPs under the operating conditions [17,18]. The trend of mean Au size was consistent with the order of C–Br BDEs, following $\text{C–Br}_{\text{C}_3\text{H}_7\text{Br}} < \text{C–Br}_{\text{CH}_2\text{Br}_2} < \text{C–Br}_{\text{CHBr}_3} < \text{C–Br}_{\text{CBr}_4}$ [29,30].

Table 2

Relative chemical composition of the Au catalysts. Elemental concentrations are expressed as atomic percentage.

Catalyst	Atomic ratio of Au species (%)			Au 4f _{7/4} BE (eV)		
	Au ³⁺	Au ⁺	Au ⁰	Au ³⁺	Au ⁺	Au ⁰
Sintered	0	28.5	71.5	–	84.6	84.1
Redispersed*	11.4	68.2	20.4	86.2	84.8	83.9

*Sintered Au/AC redispersed with CHI_3 at 40 °C for 60 min.

Upon treatment using equivalent chlorohydrocarbons, the Au diffraction features did not significantly change when using

Fig. 5. (a) XRD patterns of sintered Au/AC catalysts and after treatment with a series of bromohydrocarbons at 40 °C for 12 h; (b) Corresponding Au average particle size of the sintered Au/AC before and after redispersion indicated in (a).

Fig. 6. (a) XRD patterns of the sintered Au/AC catalysts and after treatment with a series of chlorohydrocarbons at 40 °C for 12 h; (b) Corresponding Au average particle size of the sintered Au/AC before and after redispersion indicated in (a).

C₃H₇Cl and CH₂Cl₂ (Fig. 6). In the cases of CHCl₃ and CCl₄, the intensities of the Au diffraction features decreased. Similar to bromohydrocarbons, the redispersion efficiency of chlorohydrocarbons was consistent with the variation in C–Cl BDEs, accompanied by the order: C–Cl_{C₃H₇Cl} < C–Cl_{CH₂Cl₂} < C–Cl_{CHCl₃} < C–Cl_{CCl₄} [29,30].

To clarify the redispersion processes, we modeled the Au NPs as spherical drops [31]. The R_s and R_D are indicated as the curvature radius of the sintered and redispersed Au NPs, respectively (Fig. 1). The redispersion rate, Δr , was defined as the change in mean size diameter per unit time. Thus, the redispersion rate was affected by the treatment temperature and time, as well as by the nature of the C–I bond when excluding the effect of the carrier [36,37]. The C–X (X = Cl, Br, and I) BDE data used in this work were collected from previous experiments

and reported data [28–30]. Using all three alkyl halides, namely, chloro-, bromo-, and iodohydrocarbons, the plots of redispersion rate against C–X BDEs at the indicated treatment temperature and time are shown in Fig. 7. A good linear relationship with $R^2 = 0.9502$ was achieved. The redispersion rate decreased with increasing C–X (X = Cl, Br, and I) BDEs of the halohydrocarbons. The highest redispersion rate was achieved using CHI₃ as indicated by the minimum BDE_{C–I}. In general, iodohydrocarbons exhibit BDE_{C–I} lower than BDE_{C–Br} and BDE_{C–Cl} of bromohydrocarbons and chlorohydrocarbons, respectively. Thus, a distinct dividing zone was observed in Fig. 8, indicating a decrease in redispersion rate following the order of BDE_{C–I} > BDE_{C–Br} > BDE_{C–Cl}.

For the redispersion mechanism, taken a CHI₃ as example, when the sintered Au/AC catalyst was immersed in CHI₃ solution, a monolayer of iodic species was subsequently and spon-

Fig. 7. Relative catalytic activity of acetylene hydrochlorination over the Au/AC catalyst before and after regeneration cycles with various redispersion treatments with CHCl₃, CHBr₃, and CHI₃ (three regeneration cycles).

Fig. 8. Correlation plots of the dependence of C–X (X = I, Br, and Cl) BDEs of halohydrocarbons on the redispersion rate of Au NPs at 40 °C, derived from variations in radius of Au NPs before and after treatment with a series of halohydrocarbons.

taneously adsorbed on the surfaces of large Au NPs in iodic solution [40]. As a result of electron donation, Au NPs underwent fusion and fragmentation in the solution. Adsorption of iodic species on Au NPs also decreased the surface potential, therefore inducing redispersion in a controlled manner in the solution and subsequently on the solid support [10,40]. The spontaneous chemisorption of iodic species on Au NPs was confirmed by electrochemistry results and optical spectra [24]. The effect of iodohydrocarbons on the dispersion of Au NPs was mainly controlled by the C–I bond strength, which was strongly correlated with the concentration of the active iodic species. Activated carbon was selected as the support for Au due to the fact that the interaction between carbon and Au NPs was relatively weak. The existence of weakly bound Au was supported by the variation in the Au content following washing the catalyst with water, acetonitrile, hexane, and toluene in the absence of any halohydrocarbons [17]. Therefore, the larger Au NPs were prone to form during elevated conditions on the surface of the carbon. The principle we carried out was to use a liquid phase to redisperse the sintered larger Au NPs into smaller ones by treatment with iodohydrocarbons. Throughout the entire redispersion procedure, all NPs redispersed randomly by self-diffusion. The dissociated iodic species from iodohydrocarbons react with Au NPs on the carbon support and induce the redispersion process. Given that Au donates electrons to iodic species, large Au NPs conceivably underwent fusion and fragmentation on the support by forming Au–I species. The XPS data confirmed this hypothesis (Fig. 4). In the process of diffusion, Au deposition on the carbon surface could be due to differences between the reduction potential of the intermediate Au_xI_y and the oxidation potential of the rich oxygenated-functional surface of the carbon. Therefore, the spontaneous deposition of Au NPs on the carbon support during redispersion was ascribed to the redox reaction between carbon and Au_xI_y intermediates, which was similar to the reaction mechanism between Pt NPs and single-walled carbon nanotubes or graphene oxide [38,41].

The effects of the support on the redispersion behavior of the sintered Au catalysts have been explored in a previous work [18]. The study indicated that the use of CHI_3 treatment could redisperse the sintered Au NPs on carbon materials, such as XC-72 and carbon nanotubes (CNTs), as well as on oxide supports, like SiO_2 and CeO_2 . With the carbon carriers, XC-72, and CNTs and supported Au catalysts, Au NPs of about 30 nm in size were converted into several nanometers or clusters. In contrast, although a slight decrease was observed in the size of Au particles on the CeO_2 and SiO_2 supports. After the CHI_3 treatment, the sizes remained within the submicrometer range, which was in agreement with the similar observation of the redispersion behavior by Sá et al. [15].

As an effective regeneration protocol, the performance of the redispersed Au catalyst was tested for acetylene hydrochlorination. All catalytic reaction results were obtained after 4 h of operation when the steady state was attained (Fig. 8). The results revealed that acetylene conversion of the as-prepared Au/AC decreased from 81.8% to 11.2% over the sintered sample. The selectivity to VCM was higher than 99% for all the cat-

alysts examined. The catalytic activity of the sintered Au/AC treated with CHCl_3 , CHBr_3 , and CHI_3 showed different extents of recovery. However, acetylene conversion was marginally lower than that of the as-prepared catalyst, which could be attributed to the loss of some Au during redispersion [42,43]. The regenerated Au/AC by CHI_3 exhibited the highest acetylene conversion over both counterparts obtained from CHCl_3 and CHBr_3 , even after three regeneration circles. Consequently, the Au/AC catalysts can be used over a number of deactivation-regeneration cycles with negligible deterioration in catalytic performance.

Finally, the dispersion mechanism of Au NPs was proposed. In general, with the CHI_3 treatment as the classic approach, the fundamental procedures can be interpreted in four steps: chemisorption, disintegration, redispersion, and formation of small nanoclusters on the carriers. The rapid chemisorption and interaction of iodohydrocarbons on the surface of large Au NPs initially occurred, resulting in the homolysis of the C–I bond [24,44]. Halide radical/ions were adsorbed on the Au surfaces with binding energies that scale with polarizability ($\text{I} > \text{Br} > \text{Cl}$) and crystal facet $\{ (111) > (110) > (100) \}$ [23]. The second step involves fast homolysis dissociation of the C–I bond on the Au surface, following slow disintegration and diffusion of main Au particles to form Au–I species. Further disruption was sustained by the ongoing interaction of iodic species with the main Au particles. Subsequently, the particles rapidly dispersed to their final size and reduced the surface potential energy. The final particle size was affected by the complete consumption of the large Au NP precursors after a long term treatment with CHI_3 [24,45]. Generally, iodo-, bromo-, and chlorohydrocarbons functionally serve in a similar manner during the redispersion of the sintered Au/AC catalysts but gave different redispersion rates. The redispersion rate was determined by the variation in $\text{BDE}_{\text{C-X}}$ ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$) in the halohydrocarbons with a strong dependence. Consequently, the proposal is suggested that the $\text{BDE}_{\text{C-X}}$ ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$) can be used as a descriptor for the reverse agglomeration of sintered Au/AC to predict the redispersion of sintered Au NPs.

4. Conclusions

We developed a facile and rapid protocol for the redispersion of sintered Au/AC catalysts, and used the C–X ($\text{X} = \text{I}, \text{Br}, \text{and Cl}$) BDEs as a predictive descriptor. Upon treatment with halohydrocarbons, large Au particles exhibited redispersion under mild and safe conditions. The correlation of the C–X BDEs of halohydrocarbons with the redispersion rate showed that the lowest BDE exhibited the best efficiency of redispersion. This finding would facilitate redispersion and regeneration of Au-based catalysts supported on carbon-based hosts. The mechanism gave a molecular level understanding of the critical interfacial events and revealed a strategy for the production of smaller Au NPs/cluster.

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Graphical Abstract

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C–X (X = Cl, Br, I) bond dissociation energy as a descriptor for the redispersion of sintered Au/AC catalysts

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The study proved that alkyl halide induces the redispersion of sintered Au NPs based on R–X (X = I, Br, Cl) bond dissociation energies and thus provides a simple descriptor for the regeneration of inactive supported Au catalysts.

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C-X (X = Cl, Br, I) 键解离能作为烧结Au/AC 催化剂再分散的描述因子及相关蕴意

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摘要: 负载型 Au 基催化剂在工业过程中具有非常广泛的潜在应用, 如催化加氢/脱氢过程、精细化学品合成、能源催化转化及环境保护等过程, 表现出很高的催化活性和选择性. Au 基催化剂活性物种或活性中心基本由纳米粒子或化合物构成, 但在应用过程中因 Ostwald 熟化效应或粒子迁移作用, 尤其是高温高压等苛刻反应条件下, 均随应用时间延长从小尺寸粒子逐渐长为大粒子, 造成活性降低或完全失活, 这也是负载型催化剂失活的最主要原因之一. 其中因成本、稀缺等特性, 负载型 Au 催化剂的烧结问题是影响和制约其应用的主要因素. 除可通过载体改性、助剂和官能团配位稳定等方法来延缓其失活过程外, 对已烧结催化剂的高效、快捷和绿色的再分散/再生过程也具有基础和应用研究的重要意义.

活性炭载 Au 催化剂 (Au/AC) 广泛应用于乙炔氢氯化反应中, 以期替代高毒性的汞基催化剂, 但在反应过程中因高活性的 Au^{3+} 物种易被还原而形成 Au^0 物种进而烧结导致失活; 如新鲜 Au/AC 催化剂表面的 Au 粒子尺寸为 1–2 nm, 经乙炔氢氯化反应后变为 33 nm 左右; 随之在 453 K、0.1 MPa、乙炔体积空速 (GHSV) 为 600 h^{-1} 、氯化氢与乙炔摩尔比为 1.1 的反应条件下, 乙炔转化率从 81.8% 降至 11.2%. 如何有效对大粒子 Au 再分散/再生可为其应用提供有力支撑. 有研究表明, 气相 CH_3I 在甲醇羰基化反应过程中明显改变 Au/AC 表面的 Au 粒子尺寸; 或采用浓盐酸或王水也可将烧结的 Au/AC 催化剂进行再分散/再生. 但已有的 Au 基催化剂再分散/再生过程均伴随着强酸、强氧化或高毒性在分散剂的应用, 对环境的影响及后续处理有明显的局限性, 且再分散机理尚不明确.

在前期工作基础上, 本文采用系列卤代烃 (碘代烃、溴代烃和氯代烃) 对烧结的 Au/AC 进行再分散/再生研究. 结果表明, 在室温常压条件下 CHI_3 可以快捷高效地对烧结 Au/AC 催化剂进行再分散/再生, 具有最优的再分散性能; 通过对系列碘代烃 C–I 键的解离能分析, 发现 C–I 解离能越低越有利于大粒子 Au 的再分散. 同时, 溴代烃和氯代烃对烧结的 Au/AC 催化剂也具有再分散能力, 但比碘代烃的再分散效率低. C–X 键的解离能与再分散效率有强相关性, 即 C–X 键的解离能越低越有利于 Au 的再分散. 总体上, 三类卤代烃再分散效率高低顺序为 $\text{C–I} > \text{C–Br} > \text{C–Cl}$. 进而, 通过不同分散过程中 Au 粒子分散状态推测了卤代烃对 Au 粒子的再分散机理, 即卤代烃先在 Au 粒子表面化学吸附, 然后 C–X 键解离, 形成 Au–X 物种, 小粒子 Au 在 AC 表面聚集并稳定, 最后形成高分散 Au 粒子 (粒径 $< 1 \text{ nm}$) 催化剂. 以乙炔氢氯化反应考察了再生 Au/AC 催化剂性能, 结果表明, 该催化剂上乙炔转化率可达 79.4%, 基本恢复至初始水平, 且该方法可对失活催化剂进行多次高效再生.

关键词: 金; 纳米粒子; 再分散; 卤代烃; 乙炔氢氯化

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