PtNi bimetallic structure supported on UiO-67 metal-organic framework (MOF) during CO oxidation

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1. Introduction

Bimetallic nanoparticles (BNPs) often show different electronic and chemical properties from their monometallic parents, enabling catalysis with improved selectivity, activity and stability [1,2]. Insights into the origin of these intriguing properties have been the subject of many theoretical and experimental studies, aimed at understanding the synergy between the bimetallic phases, and thus enabling the rational design of highly active and selective catalytic systems [3–5]. For example, in catalytic oxidation of alcohols (to aldehydes) over a bimetallic AuPd/TiO\textsubscript{2} catalyst, Au acted as an electronic promoter for Pd and improved the turnover frequency, TOF (up to 270,000 h\textsuperscript{-1}) and selectivity in comparison with the monometallic Au/TiO\textsubscript{2} and Pd/TiO\textsubscript{2} catalysts [6]. BNPs, such as PtRe and PtIr supported on Al\textsubscript{2}O\textsubscript{3} catalysts, have gained strong commercial interest since the 1960\textsubscript{s} for their use in hydrocarbon reforming, which has stimulated a large number of investigations on possible yet practical applications of different BNPs [7–9]. Currently, supported BNPs catalysts, composed of a transition metal (e.g., Ni, Ru and Cu) together with Pt, are widely used in, for example, oxidation [10], hydrogenation [11] and electro-catalysis (for fuel cell applications) [12]. Compared to the respective monometallic catalysts, these BNPs catalysts have more complex structures such as alloys, crystalline, Janus and core-shell arrangements. Additionally, structural variations of bimetallic phases under reaction conditions are expected to occur [13–15]. For example, dynamic variation of PtNi BNPs (supported on carbon black) under oxidising and reducing conditions was studied using in situ X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD). Specifically, both in situ techniques confirmed that, under the oxidising conditions, the outward diffusion of Ni was induced to form a NiO-rich surface on Pt phase, whereas under reducing conditions inward diffusion of Ni occurred, thus producing a Pt-rich surface [16,17]. These findings clearly show the necessity of in situ and operando studies to understand the structure-reactivity correlations in BNPs since their structures can alter significantly under reaction conditions. Over the past decades, efforts have been made to understand the nature, as well as the behaviors under reaction conditions, of such BNPs. For example, detailed X-ray absorption near edge spectroscopy (XANES) studies by Bao...
et al. showed the formation of NiOx-Pt(111) and NiOx-Pt-Ni-Pt(111) surface structures in PtNi BNP catalysts supported on carbon black at reduction temperatures of 423 K and 523 K, respectively. Such ultrathin Ni oxide overlayers (NiO) over Pt metal, which contain coordinately unsaturated ferrous (CuF) sites, are believed to enhance the catalytic activity of the BNPs in CO oxidation (1% CO, 20% O2 and 79% He) [18]. Atomic layer deposition (ALD) method was employed to selectively deposit NiO phase on the Pt phase of model Pt supported on Al2O3 thin film (i.e., NiO/Al2O3), which showed comparatively high catalytic activity and thermal stability than the monometallic Pt/Al2O3 in CO oxidation [19]. Based on XANES characterisation, the enhanced catalytic activity was proposed to be due to the NiOx-Pt interface created by ALD, in which NiO acts as the promoter. In addition to the proposed synergistic effects, the geometric and structural aspects of BNPs also play an important role in the improved measurement in activity and stability [20,21]. For example, Cheng et al. [22] reported a size-dependent activity in catalytic dehydrogenation of formic acid over AuPd BNPs supported on activated carbon. Specifically, TOF increased from 14 h−1 to 718 h−1 with a decrease of the size of AuPd BNPs from 12.8 ± 0.5 nm to 3.8 ± 0.5 nm.

It is known that the appropriate selection of catalyst supports (hosts) with well-defined porosity and high surface area contributes to the formation of well-dispersed small NPs (of 1–3 nm) for catalysis [23,24]. Metal-organic frameworks (MOFs) have well-defined cavities and functionalisable chemical/physical properties, which can accommodate a variety of guest species. The porous crystalline framework of MOFs can enable spatial segregation and confinement of metal NPs, and hence avoid the aggregation of NPs under reaction conditions. These features, along with the exceptionally available choices of both organic and inorganic components to construct MOFs, allow the possibility of rational design of supported catalysts on MOFs with precise control over many variables [25–27]. A recent study on monometallic Pt NPs supported on UiO-67 MOF showed that, in comparison with the conventional metal oxide supports such as ZrO2, UiO-67 enhanced the structural confinement and limited the sintering of Pt NPs under oxidising conditions [28].

Many MOFs have been used to prepare supported BNPs due to their highly porous structures and the associated confinement effect on restricting the growth of BNPs [29–31]. For example, ultrafine AuNi BNPs with an average size of 1.8 nm were successively immobilised on MIL-101 by a double solvent method. The resulting supported BNPs showed a high activity for hydrogenation (H2) generation from the catalytic hydrolysis of ammonia borane [32]. In addition, cascade catalysis over BNPs@MOF catalysts with three active sites (i.e., acid/base-NP1-NP2) has also gained interest, taking advantage of not only the synergy between BNPs but also the intrinsic active sites in MOFs [33]. For example, a PdAg@MIL-101 catalyst showed excellent catalytic activity (i.e., complete conversion) and selectivity in one-pot cascade conversion of nitrilotere to the secondary arylamine [34]. Although the formation of relevant bimetallic structures in MOFs can enable spatial segregation and confinement of metal NPs, and hence avoid the aggregation of NPs under reaction conditions. These features, along with the exceptionally available choices of both organic and inorganic components to construct MOFs, allow the possibility of rational design of supported catalysts on MOFs with precise control over many variables [25–27]. A recent study on monometallic Pt NPs supported on UiO-67 MOF showed that, in comparison with the conventional metal oxide supports such as ZrO2, UiO-67 enhanced the structural confinement and limited the sintering of Pt NPs under oxidising conditions [28].

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was performed during catalyst exposure to a mixture of CO:O₂ (CO/O₂ ratio = 2, total pressure = 3 mbar) at RT before it was heated to 300 °C for 1 h in a reducing environment with the H₂ (10 vol%)/Ar flow (at 100 ml min⁻¹). Previous work has shown that the condition was sufficient to fully reduce the catalyst [28]. After reduction, the reactor was firstly cooled down to RT under Ar flow (at 100 ml min⁻¹), then the temperature was ramped from RT to 410 °C at a heating rate of 6 °C min⁻¹ under a reacting flow (CO/O₂ = 2, Ar as balance, total flowrate = 100 ml min⁻¹) to perform the catalysis. The bed temperature was measured by a K type thermocouple adjacent to the catalyst bed. After each run, the furnace was turned off to allow the reactor to cool down to RT under Ar (at 100 ml min⁻¹). Mass spectrometry (MS) of the outlet gas was performed using an HPR20 QIC mass spectrometer (Hiden Analytical). During the light-off experiments, the spectrometer continuously monitored the ion currents at a mass-to-charge ratio (m/e) of 36, 32, 28 and 44, corresponding to signals of Ar, O₂, CO and CO₂, respectively.

3. Results and discussions

The resulting catalysts were fully characterised using XRD, SEM and N₂ physisorption, showing that the integrity of UiO-67 framework was maintained after metal loading (Figs. S1 and S2, Table S1). ICP-OES analysis showed that the actual metal loadings match the theoretical values for all the catalysts. Comparative assessment of the catalytic activity of the catalysts was performed using CO oxidation with a stoichiometric CO/O₂ mixture (at 100 ml min⁻¹). Fig. 1a shows the comparative light-off behaviour of the catalysts under investigation. Clearly, (i) the BNP PtNi@UiO-67 catalyst demonstrated exceptionally good performance in CO oxidation in comparison to the control monometallic catalysts and, (ii) the Ni@UiO-67 catalyst was the least active among the three catalysts under investigation. Specifically, T₁₀%, T₅₀% and T₉₀% (temperatures at which CO reach 10, 50 and 90% conversion, respectively) of the BNP PtNi@UiO-67 catalyst were at 121 °C, 161 °C and 171 °C, respectively, and were much lower than that of the monometallic Pt@ UiO-67 and Ni@UiO-67 catalysts (e.g., T₁₀% = 225 °C for Pt@UiO-67 and T₅₀% = 388 °C for Ni@UiO-67). The catalytic experiments were performed up to temperatures of 410 °C (at ramp rate of 6 °C min⁻¹). The monometallic Ni@UiO-67 catalyst showed incomplete CO conversion (16%) at 405 °C. Importantly, PtNi@UiO-67 also demonstrated a good stability in the cyclic deactivation tests (Fig. 1b), showing insignificant changes in T₁₀%, T₅₀% and T₉₀% temperatures at 123 ± 2 °C, 164 ± 3 °C and 174 ± 3 °C, respectively, over four cycles of catalysis (as shown in Fig. S3). These results are in line with our previous findings, suggesting that the porous structure of UiO-67 MOF prevented sintering of the supported Pt NPs, and hence the anti-deactivation of the catalyst under oxidising conditions [28]. Additionally, for the BNP PtNi@UiO-67 catalyst, the metal NP mobility might also be reduced due to PtNi alloying, as reported by Colón-Mercado et al., who showed that the anchoring effect of Ni to Pt on carbon substrates (e.g., carbon black) limits the mobility of Pt NPs due to strong bonding of Pt atoms to carbon substrates through bridges of Ni atoms [37].

In order to elucidate the enhanced activity of the BNP catalyst, the surface chemistry of the Ni@UiO-67 and PtNi@UiO-67 catalysts in CO oxidation were investigated using in situ XPS under NAP conditions (CO/O₂ ratio = 2, total pressure = 3 mbar; detailed NAP-XPS...
study of CO oxidation over Pt@Uio-67 was reported in our previous work [28]. Before catalysis under the NAP conditions, the as-synthesised catalysts were reduced in situ under H2 at 1 mbar H2. Fig. 2 shows the dynamic variation of surface metallic phases in the two catalysts during reduction. For the monometallic Ni@Uio-67 catalyst, Ni 2p XPS spectra shows full reduction of the supported Ni2+ species to metallic Ni at 300 °C which was evidenced by the appearance of the doublet of metallic Ni (Ni 2p3/2 at ~852.5 ± 0.1 eV) at ~300 °C. Conversely, regarding the bimetallic PtNi@Uio-67 catalyst, annealing in H2 up to 300 °C only led to the partial reduction of the Ni species (i.e., 38% metallic Ni versus 62% Ni oxides, as shown in Fig. 2b. Note: variation in spectra quality of Ni 2p region in Fig. 2 was due to the different metal loadings in the monometallic and bimetallic catalyst). By increasing the reduction temperature further to 360 °C, only ~72% Ni phase was reduced (Fig. S4). The findings show that it was comparatively difficult to reduce Ni oxides in the presence of Pt species. Fig. 2c shows the full reduction of Pt species to metallic Pt at 300 °C in the BNP PtNi@Uio-67 catalyst. Interestingly, the Pt 4f7/2 peak in the reduced bimetallic catalyst centred at a binding energy (BE) of 70.4 eV, i.e., lower than that of monometallic Pt NPs (at 71 eV) [28]. A rational explanation for the relatively low BE measured for Pt 4f in PtNi@Uio-67 could be the charge transfer between the metallic Pt and Ni oxide, suggesting an adjoining configuration of Pt metal and Ni oxide phases in the BNP catalyst, leading to the observed difficulty in reducing the Ni species. Specifically, the

Fig. 1. (a) Comparative light-off curves of CO conversion over the monometallic and bimetallic catalysts, (b) T10%, T50% and T90% values of the BNP PtNi@Uio-67 catalyst in the cyclic deactivation experiments (reaction conditions: heating ramp = 6 °C min⁻¹, atmospheric pressure, total flowrate = 100 ml min⁻¹, CO/O2 = 2, Ar as balance).

Fig. 2. NAP-XPS spectra of (a) Ni 2p of Ni@Uio-67, (b) Ni 2p of PtNi@Uio-67 and (c) Pt 4f of PtNi@Uio-67 at different reducing temperatures and 1 mbar H2.
charge transfer between Pt and Ni stabilised a thin layer of NiO$_x$ on top of the metallic Pt phases. Relevant charge-transfer stabilisation has been observed in model catalyst systems of 2D oxide films on single crystal metals (e.g., cobalt oxide on Au and iron oxide on Pt) [38,39]. However, such phenomena have not yet been measured for real catalysts.

During CO oxidation, under the NAP condition at a total pressure of 3 mbar (CO/O$_2$ = 2), surface dynamics of the Ni@UiO-67 and PtNi@UiO-67 catalysts were investigated by XPS coupled with simultaneous MS analysis. CO conversion data from the temperature-programmed reaction along with the corresponding XPS measurements of Pt 4f and Ni 2p regions of the catalysts are shown in Fig. 3. It should be noted that the difference between the measured CO conversions from the light-off and NAP-XPS experiments was attributed to the different configurations of the two systems, as shown previously [28]. By monitoring Ni 2p core level spectra of the reduced Ni@UiO-67 catalyst during catalysis under NAP conditions, we observed the oxidation of metallic Ni upon exposing the catalyst to the CO/O$_2$ mixture at 3 mbar. No CO conversion was observed at temperatures < 150 °C, while the catalytic turnover took place on active NiO surfaces at > 150 °C (Fig. 3a and 3d). When the bimetallic catalyst was exposed to the CO/O$_2$ mixture < 150 °C, the partially reduced Ni metal was oxidised, while metallic Pt remained under the conditions used (Fig. 3b and 3c). A previous study on supported Pt NPs on UiO-67 MOF showed a BE shift of Pt 4f$_{7/2}$ from 71.2 eV (metallic state) to 71.8 eV due to the adsorption of CO on metallic Pt surfaces at relatively low temperatures (<200 °C) [28]. One explanation as to why the phenomenon did not occur in the bimetallic catalyst might be attributed to the passivation of Pt metals by a layer of NiO$_x$, suggesting a core-shell structure for the PtNi BNPs under the conditions used. In this case, Pt metal mostly diffuses into the core of the BNPs while NiO$_x$ segregates to the surface of the BNPs due to the lower surface energy of Ni oxides than that of Pt metal. Previously, metal oxide-Pt interfaces of BNPs, such as FeO$_x$-Pt(111) [40] and NiO$_x$-Pt interface [19] structures, were proposed as the active phases for CO oxidation. Additionally, herein, based on the findings from the NAP-XPS analysis, we also propose that the NiO$_x$ ultrathin layer stabilised on the metallic Pt was the possible active phase responsible for the active bimetallic PtNi@UiO-67 catalyst (Fig. 3b and 3c) in comparison with the bulk NiO in the monometallic Ni@UiO-67 catalyst (Fig. 3a). Density functional theory (DFT) calculations on different PtNi model structures (i.e., NiO$_x$-Pt, Pt(111) and NiO/Pt) showed that the activation energy barrier ($E_a$) of CO oxidation over the NiO$_x$-Pt model structure was the lowest (0.37 eV) in comparison with others (i.e., 0.86 eV for Pt(111) and 1.08 eV for NiO/Pt, respectively) [41], supporting the experimental findings by this work (Fig. 1a and Fig. 3d).

To confirm the hypothesis derived from the NAP-XPS study of CO oxidation over the catalysts, we performed HR-STEM analysis.

Fig. 3. Temperature programmed CO oxidation over the Ni@UiO-67 and PtNi@UiO-67 catalysts under NAP-XPS conditions (CO/O$_2$ ratio = 2, total pressure = 3 mbar): (a) Ni 2p spectra of Ni@UiO-67, (b) Ni 2p spectra of PtNi@UiO-67, (c) Pt 4f spectra of PtNi@UiO-67; and (d) CO conversion by MS for the monometallic and bimetallic catalysts at different reaction temperatures.
on three exemplar catalysts. The as-reduced monometallic Ni@UiO-67, as-reduced BNPs Ni/Pt@UiO-67 and used BNPs PtNi@UiO-67 (from the catalysis under the plug-flow conditions) were all imaged, and the results are shown in Fig. 4. Fig. 4a (i.e., HAADF images of the samples) confirms that, for the as-reduced catalysts under investigation (i.e., the fresh catalysts), (i) metal NPs are incorporated within the MOF matrix and (ii) the distribution of metal NPs throughout the individual MOF particle appears to be uniform. High magnification images of the monometallic Ni NPs show that they are relatively large, polycrystalline particles with a diameter of > 10 nm. Lattice resolution images show a characteristic fringe spacing of 2.02 ± 0.08 Å (average of 8 measurements on 8 different particles), which is consistent with the (200) plane in rock-salt NiO [42]. In contrast, the BNPs supported on UiO-67 show a very different morphology (Fig. 4c and 4d), with much smaller particles at ~ 2 nm, which appear to be single crystalline and have remarkable monodispersity. Lattice resolution images show a characteristic spacing of 2.33 ± 0.07 Å, which is consistent with (111) planes in metallic Pt [43]. There were no apparent differences in the morphology or crystal structure observed between the freshly reduced (Fig. 4c) and used (Fig. 4d) PtNi@UiO-67 catalysts. A more comprehensive set of HAADF images for the three catalyst samples studies is shown in Fig. S5.

EDX spectroscopic maps were taken of small groups of the freshly reduced PtNi@UiO-67. A representative set of maps is shown in Fig. 4e (four more maps are shown in Fig. S6). The maps of the Pt L\text{a} and Ni K\text{a} peaks confirm that Ni and Pt are co-located within single particles and the overlay image is suggestive of a core-shell structure (the Ni maps are in general more diffuse and larger in spatial extent for a given particle), confirming the hypothesis proposed according to the findings from the NAP-XPS characterisation. Furthermore, comparative EDX spectra formed by averaging over an entire particle (64 pixels) and the same size area from a section of MOF (where there are no metal particles) confirm that there is no detectible Ni or Pt dispersed on the MOF matrix, i.e. it is all localised in the particles (Fig. S7).

To further confirm the proposed core-shell NiO\textsubscript{x}-Pt structure within the MOF matrix, radial averages of 18 particles were taken for both the Pt and Ni EDX maps. A radial average displays normalised counts from the centre of the particle to its surface, taking into account all pixels within the particle (a radial profile begins in the centre of the particle, stepping out incrementally pixel-by-pixel and taking the average intensity of all pixels at a certain radius. A further description of the method is described elsewhere [44]). The expected behaviour for a radial average of a core-shell particle is that the core element will decay smoothly from the central

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**Fig. 4.** STEM images: (a) HAADF images of the fresh PtNi@UiO-67 catalyst at low magnification showing a single UiO-67 particle (hosting the metal NPs) and a higher magnification image showing individual PtNi BNPs within the MOF; (b) lattice resolution HAADF image of a freshly reduced monometallic Ni catalyst particle; (c) lattice resolution HAADF images of freshly reduced PtNi BNPs - scale the same for all four images; (d) lattice resolution HAADF images of used PtNi BNPs; and (e) EDX maps of freshly reduced PtNi BNPs supported on UiO-67 MOF, showing distribution of Pt and Ni phase in the matrix of the MOF.
position and the shell element will display a more complex structure with a plateau in the central region and a maximum further out (where the electron beam is going solely through the shell and not the core) [45]. An example of a radial average from a single particle which shows this behaviour very clearly is seen in Fig. 5a. To confirm that this core-shell structure is present in most if not all particles, the radial averages from 18 different particles were combined in Fig. 5b, where the averaged trace also shows the characteristic core-shell behaviour. The radial averages suggest that the NiO x shell thickness is extremely thin, i.e., <5 Å, which may explain why no shell is clearly discernible on the Pt cores in the HAADF images (Fig. 4c and 4d), in addition to the fact that Ni and O have a much lower atomic number than Pt and so will be of much lower intensity in the HAADF images. Regarding the probe size of STEM, it was approximately 1 Å full width half maximum before interaction with the sample. However, beam broadening due to scattering through the support material could increase this size considerably. In the centre of the MOF particles, the electron beam might pass through approximately 200 nm of UiO-67, which could result in beam broadening so that 90% of the probe was contained in a circle of diameter of approximately 5.4 nm at the exit surface of the MOF particle [46]. The average width of the beam through the sample at the centre point was therefore approximately 2 nm [46]. At the edge of the MOF particle, where the data were collected, beam broadening was substantially lower due to the relatively low thickness of the MOF. We cannot accurately determine the probe diameter at all points but note that atomic columns could be observed in the ADF images of all particles imaged, which would place a maximum on the probe diameter of approximately 2 Å. This is approximately equivalent to the pixel size used in the EDX maps, which will have a resolution of 2–3 times the pixel size (approximately 5 Å).

Accordingly, combining the findings from the HR-STEM and NAP-XPS analyses, we propose that the operando surface structure is a charge-transfer stabilised NiO x monolayer over a Pt metallic core, much like the charge transfer stabilised films of FeO and CoO which have been observed on single crystals [38,39]. More importantly, in contrast to the results of Mu et al. [18], we found that under operando conditions the metals are fully phase-separated, i.e., no metallic Ni remains alloyed with the Pt core, and this was evidenced by the absence of a metallic Ni peak during the XPS analysis of the catalyst under the operando conditions. It also worth noting that it is generally accepted that the structural variation and the formation of the thermodynamically stable structures in bimetallic phases are related to the chemical environment present on the surface. Density functional theory (DFT) calculations, as well as experimental results, of the bimetallic Pt-M catalysts shows that M – Pt – Pt (M represents Ni, Co and Fe) is the most thermodynamically stable structure under the oxidising environment due to the lower surface energy of transition metals than that of Pt metal (i.e., thermodynamic potential for segregation, $\Delta E_{seg}$, is negative) [47,48]. Accordingly, NiO x segregates on Pt metal surface can be attributed to the Ni-Pt-Pt structure, which is thermodynamically preferred configuration in the Ptni@UiO-67 catalyst under the conditions used in this work.

4. Conclusions

Understanding the behaviour of bimetallic nanoparticles (BNPs) under reaction conditions is crucial to progress the development and application of these catalysts. Herein, a well-dispersed Ptni BNP supported on UiO-67 catalyst was prepared (i.e., Ptni@UiO-67) and studied to gain insight into its intrinsic structural and catalytic properties. Comparative light-off experiments of catalytic CO oxidation were performed over the Ptni@UiO-67 and monometallic control catalysts (i.e., Pt@UiO-67 and Ni@UiO-67), which showed the synergistic effect of Ptni BNPs through a much improved catalytic activity in comparison with the control (e.g., $T_{10\%} = 121$ °C for Ptni@UiO-67 versus $T_{10\%} = 223$ °C and 388 °C for Pt@UiO-67 and Ni@UiO-67, respectively). Under reducing conditions (1 mbar $H_2$), NAP-XPS characterisation revealed (i) the resistance of NiO x phase to reduction for the bimetallic particle compared with monometallic system and (ii) the anomalously low binding energy of Pt 4f in Ptni@UiO-67, which suggested a core-shell bimetallic configuration and stabilisation of the NiO x phase by Pt via charge transfer. The NiO x shell-metallic Pt core structure of the supported BNPs was then confirmed by comprehensive post-mortem HR-STEM analysis. Accordingly, based on the findings, it was proposed that the stabilised shell NiO x phase in Ptni@UiO-67 is responsible for the measured improvement in its catalytic activity in CO oxidation. It is worth mentioning that we cannot rule out interfacial sites existing (as the current techniques employed cannot determine whether the NiO x shell was complete or not), and they may indeed also be active. Accordingly, further investigation to gain the insight into this aspect is needed.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.