Surface Enrichment of Pt in Stable Pt-Ir Nano-alloy Particles on MgAl_2O_4 Spinel in oxidizing atmosphere

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Supporting Information

ABSTRACT: With the capability of MgAl_2O_4 spinel {111} nano-facets in stabilizing small Rh, Ir and Pt particles, bimetallic Ir-Pt catalysts on the same support were investigated, aiming at further lowering the catalyst cost by substituting expensive Pt with cheaper Ir in the bulk. Small Pt-Ir nano-alloy particles (< 2nm) were successfully stabilized on the spinel {111} nano-facets as expected. Interestingly, methanol oxidative dehydrogenation (ODH) rate on the surface Pt atoms increases with oxidizing aging but decreases upon reducing treatment, where Ir is almost inactive under the same reaction conditions. Up to three times enhancement in Pt exposure was achieved when the sample was oxidized at 800 °C in air for 1 week and subsequently reduced by H_2 for 2 h, demonstrating successful surface enrichment of Pt on Pt-Ir nano-alloy particles. A dynamic stabilization mechanism involving wetting/nucleation seems to be responsible for the evolution of surface compositions upon cyclic oxidizing and reducing thermal treatments.

The superior catalytic performances make supported precious metal (PM) catalysts unsubstitutable in many practical applications. Bimetallic catalysts demonstrate great benefits not only in enhancing the catalytic performance for a specific reaction but also in reducing the cost of PMs. For example, bimetallic Pt-Ir, Pt-Re and Pt-Sn catalysts are used in petroleum reforming units to convert alkanes and cycloalkanes to aromatic hydrocarbons to achieve higher octane value [1]. Pt-Rh is widely used in oxidation of ammonia and three-way catalysts (TWCs) for the abatement of automotive exhaust emissions by oxidation of hydrocarbons, CO and nitrogen oxides (NO_x) simultaneously [2-4]. Pt-Pd is used in diesel oxidation catalysts (DOCs) to fully oxidize hydrocarbons, CO and NO [5]. Pt-Ir also attracts much attention for hydrogenation ring-opening, hydrodeoxygenation, and electrocatalytic oxidation reactions [6-9]. Introduction of a second metal usually brings significant increase in activity, higher stability. However, the thermal degradation is still inevitable especially in oxidizing atmospheres at high temperatures, which requires high PM contents to maintain the desired reactivity during the operation period and increases the catalyst cost.

For supported PM catalysts, it is well known that the metal surface structure dominates the catalytic performance while the metal-support interface structure is crucial for the thermal stability. Both the surface properties and interfacial local structures can be significantly affected upon high temperatures and atmospheres [9-

11]. Cyclic oxidizing and reducing of PM catalysts by reactants at high temperatures usually induce reversible transformation between metallic and oxidized states of the metal, as well as interval alternation between metal-support and oxide-support interfaces, leading to the presence of unstable interfacial structure. As a result, an irreversible catalyst sintering process always occurs with the migration and coalescent of metal or metal oxide particles over the support [12,13]. We recently discovered that MgAl_2O_4 spinel {111} nano-facets are able to stabilize Rh, Pt and Ir nanoparticles at very small sizes (< 3 nm) with some even as single atomic species after severe aging, due to the lattice match and strong interaction between spinel {111} oxygen termination and metals/oxides [12,13]. Such advancement in stabilizing monometallic PM catalysts improves the PM utilizations and lowers the catalyst cost. Furthermore, it offers the opportunity to synthesize thermally stable bimetallic catalysts, which may have strong synergic effect for a certain reaction and/or more efficient utilization of the precious metal.

In this contribution, we report the preparation and study on the dynamic structure of the Pt-Ir prototypical bimetallic catalysts. Their thermal stabilities and the surface compositions upon thermal treatments in various atmospheres were systematically studied. We determined the particle sizes and the total metal dispersions by X-ray diffraction (XRD), transmission electron microscopy (TEM) and H_2 -chemisorption analysis. We identified the bulk compositions of small metal particles by using scanning transmission electron microscopy (STEM) and energy dispersive X-ray (EDX) mapping analysis and probe the surface Pt atoms by using methanol oxidative dehydrogenation (ODH) at a temperature as low as 80 °C, where Ir was inactive. Our results show that Pt and Ir form PtIr alloy at small particle sizes which remain stable on the spinel MgAl_2O_4 {111} nano-facets during severe aging. Pt enrichment on the surface of Pt-Ir nano-alloy particles is facilitated by high-temperature oxidizing environment instead of reducing treatment, presumably due to the difference in the dynamic wetting/nucleation effect of IrO_x /Ir and PtO_x /Pt on the spinel {111} facets.

We prepared Pt-Ir bimetallic catalysts by incipient wetness co-impregnation of MgAl_2O_4 spinel support with PtCl_4 and IrCl_3 aqueous solution. The MgAl_2O_4 spinel crystallites have cuboctahedral shape with exposing nearly identical {100} and {111} facets [12,13]. The atomic ratio of Pt to Ir was 1:4 with the total metal loading of 1 wt. %. The samples are designated as $1\text{Pt}_{0.2}\text{Ir}_{0.8}/\text{MgAl}_2\text{O}_4$ with a suffix indicating their thermal treatments as follows. Impregnated samples were dried and freshly

calced at 500 °C for 5 h (-FO) and then were reduced in 5% H₂/He at 800 °C for 2 h (-FR_{2h}). The reduced samples were subsequently aged in ambient air at 800 °C for either 1 day (24 h, “-1DO”) or 1 week (168 h, “-1WO”). Correspondingly, the aged samples were then reduced in 5% H₂/He at 800 °C for 2h (-1DR_{2h}, -1WR_{2h}) or 24 h (-1WR_{24h}). Monometallic 1Pt/MgAl₂O₄ and 1Ir/MgAl₂O₄ samples were also prepared and treated in similar ways as detailed in the Supporting Information. Total metal loading of 2 wt% is designated as 2Pt_{0.2}Ir_{0.8}/MgAl₂O₄ (Figure S2).

Figure 1. XRD patterns for 1Pt_{0.2}Ir_{0.8}/MgAl₂O₄ samples after different thermal treatments. The “#” and “*” marks indicate the diffraction peaks for metallic Ir and Pt, respectively.

We detected the crystal phases and crystallite sizes of large metal particles in the samples from their XRD patterns. As shown in Figure 1, large metallic Ir crystallites are present in all samples and the average size increases from 45.5 to 77.6 nm for the 1Pt_{0.2}Ir_{0.8}/MgAl₂O₄-FR_{2h} and -1DR_{2h} and then maintain at around 76 nm for the 1Pt_{0.2}Ir_{0.8}/MgAl₂O₄-1WR_{2h} and -1WR_{24h} (Table 1). Large metallic Pt crystallites are only detectable in the 1Pt_{0.2}Ir_{0.8}/MgAl₂O₄-1WR_{2h} and -1WR_{24h} samples with similar size of about 70 nm. There are no visible diffractions for Pt-Ir alloy [14]. We further determined the total metal dispersions for these bimetallic samples using H₂-chemisorptions. Highest metal dispersion of 32.4% is detected on the 1Pt_{0.2}Ir_{0.8}/MgAl₂O₄-FR_{2h} sample. After aging, the dispersions decrease to 25.7% and 10.8% for 1Pt_{0.2}Ir_{0.8}/MgAl₂O₄-1DR_{2h} and -1WR_{2h}, respectively, while that for the 1Pt_{0.2}Ir_{0.8}/MgAl₂O₄-1WR_{24h} with prolonged reduction period remains at 10.5% (Table 1). Both the presence of large metal particles and the decrease in metal dispersions for the bimetallic samples are very similar to those for the monometallic 1Ir/MgAl₂O₄ and 1Pt/MgAl₂O₄ samples, which are attributed to the sintering of small metal particles that are initially located on the MgAl₂O₄ spinel {100} facets during the impregnation process [13]. The retained metal dispersions indicate the presence of small metal particles, which are indeed evident in the TEM images for the bimetallic samples (Figure 2). This again is in line with those for monometallic samples. Thus, the locations for the stable small metal particles can be readily assigned to be over the MgAl₂O₄ spinel {111} facets, in accordance with our previous observations [12,13]. Taken together, similar as monometallic Pt/MgAl₂O₄

catalysts, Pt-Ir bimetallic small particles can be stabilized on the MgAl₂O₄ spinel {111} nano-facets.

Table 1. Characteristics of 1Pt_{0.2}Ir_{0.8}/MgAl₂O₄ samples upon various thermal treatments.

1Pt _{0.2} Ir _{0.8} /MgAl ₂ O ₄	Main average size (nm)			PtIr Dispersion (%)
	<i>d</i> (XRD)	<i>d</i> (TEM)		
	<i>d</i> _{Pt}	<i>d</i> _{Ir}	<i>d</i> _{PtIr}	
-FR	-	45.5	< 2	32.4
-1DR	-	77.6	< 2	25.7
-1WR	69.2	76.1	< 2	10.8
-1WR'	72.9	75.7	< 2	10.5

Figure 2. TEM images for 1Pt_{0.2}Ir_{0.8}/MgAl₂O₄: -FR_{2h} (A), -1DR_{2h} (B), -1WR_{2h} (C) and -1WR_{24h} (D). Images for large metal particles are not shown.

We further carefully characterized the structures and compositions of the small particles in these samples by using HR-STEM and EDX analysis. As shown in Figure 3A, the small metal particles in the 1Pt_{0.2}Ir_{0.8}/MgAl₂O₄-FR_{2h} sample display hexagonal projections, equaling to cuboctahedrons in shape. The EDX spectra for different particles show the coexistence of Pt and Ir metals with various atomic ratios, indicating the formation of Pt-Ir nano-alloy particles. Single atomic species of Pt or Ir were also detected as isolated bright dots in the spectra. However, EDX spectra of the bright dots are limited due to the small amount of atoms. We also performed EDX analysis on a large area in 2D mapping mode (Figure 3B, 3C). The red and green colors represent Ir and Pt elements respectively. The brightness indicates the concentration of the elements. It was found that Pt and Ir overlap each other in most area. Specifically, the EDX spectra for some selected small particles also show the co-presence of Pt and Ir, again, with various atomic ratios (Figure 3D). For the whole area, there is much higher intensity for Ir than for Pt, consistent with the higher loading of Ir in the fresh sample. For the 1Pt_{0.2}Ir_{0.8}/MgAl₂O₄-1WR_{2h} sample, small particles and single atomic species were also de-

tested (Figure 3E, 3F). Interestingly, the dominant element in large particles is Pt, while in single atomic species Ir is more enriched (Figure 3E, 3G and 3H). Unlike the high Ir to Pt intensity ratio in the fresh sample, the Ir to Pt ratios for the large particles in the aged sample is much lower. Moreover, in general, there are more single atomic species observed for the aged sample than for the fresh one. More specifically, almost every particle in the aged sample has single atomic species surrounded. But for the fresh sample only few particles have single atomic species nearby (Figure S1). To reduce the effects of sample inhomogeneity and the sampling limit for STEM, several other areas were selected for the same analysis, which gave similar results. The observed differences in local compositions and distributions in many different areas of the sample indicate a possible PM species migration over support surface. Thus understanding the surface properties is cru-

Figure 3. HR-STEM images, EDS-mapping images and composition analysis of nanoparticles for $1\text{Pt}_{0.2}\text{Ir}_{0.8}/\text{MgAl}_2\text{O}_4\text{-FR}_{2\text{h}}$ (A, B, C and D) and $1\text{Pt}_{0.2}\text{Ir}_{0.8}/\text{MgAl}_2\text{O}_4\text{-1WR}_{2\text{h}}$ (E, F, G and H).
cial.

The surface composition on the particles, a key factor that affects the catalytic performance of bimetallic catalysts, however, cannot be obtained accurately from EDX analysis. Popular techniques for determining surface compositions, such as X-ray photoelectron spectroscopy (XPS) or FTIR of CO chemisorption [15-19], unfortunately, are not applicable for analyzing these samples due to the coexistence of multiple species, such as large Pt and Ir metallic particles, and small Pt-Ir nano-alloy particles and single atomic species as well, broadening the corresponding spectra and reducing the resolutions. Here we probed the surface Pt just on small bimetal particles using methanol oxidative dehydrogenation (ODH) reaction at a low temperature where Ir does not exhibit catalytic activities. As showed in Figure 4A, at reaction temperatures below 160°C , the mass specific ODH rates (R_{ODH}) for the $1\text{Ir}/\text{MgAl}_2\text{O}_4\text{-FR}_{2\text{h}}$ is less than $0.8\text{ mol/mol}_{\text{Ir-total}}\text{-S}^{-1}$. At temperature as low as 80°C , the $1\text{Ir}/\text{MgAl}_2\text{O}_4\text{-FR}_{2\text{h}}$ is essentially inactive. However, the $1\text{Pt}/\text{MgAl}_2\text{O}_4\text{-FR}_{2\text{h}}$ has a high mass specific ODH rate of $10.5\text{ mol/mol}_{\text{Pt-total}}\text{-S}^{-1}$ at the same temperature[12,13]. Thus the ODH rates detected on $1\text{Pt}_{0.2}\text{Ir}_{0.8}/\text{MgAl}_2\text{O}_4$ catalysts at 80°C can be mainly assigned to exposed Pt atoms. Thus, we averaged the catalytic activity to total Pt atoms which is essentially an indicator of Pt dispersion. Figure 4B shows that the Pt mass specific ODH rates increase with oxidizing aging and decreases with prolonged reducing treatment. It is interesting that enhancement rather than conventional decline in the catalytic activity took place with severe oxidative aging. Similar enhancements after oxidizing treatment were also observed on catalysts with higher total metal loadings ($2\text{Pt}_{0.2}\text{Ir}_{0.8}/\text{MgAl}_2\text{O}_4$, Figure S2). The mass specific catalytic efficiency of Pt in the supported Pt-Ir bimetallic catalysts is much higher than that in the monometallic supported Pt catalysts ($13.5\text{ mol/mol}_{\text{Pt-total}}\text{-S}^{-1}$ for $1\text{Pt}/\text{MgAl}_2\text{O}_4\text{-FR}_{2\text{h}}$), showing significant improvement in Pt utilization and potential reduction in catalyst cost.

Figure 4. ODH rates for $1\text{Ir}/\text{MgAl}_2\text{O}_4$ at various reaction temperatures (A) and that for $1\text{Pt}_{0.2}\text{Ir}_{0.8}/\text{MgAl}_2\text{O}_4$ samples at 80°C (B).

The exceptional enhancements in catalytic reactivity with aging strongly indicate a significant change in the surface structure of supported Pt-Ir bimetallic particles. It is expected that the mass specific catalytic activity could be affected by both the numbers and the local structures of surface active sites. First of all, the role of Ir in the catalytic reaction needs to be identified. As shown in Figure 4A, monometallic Ir small particles are not active for the methanol ODH reaction at all temperature lower than 80°C . However, the Pt mass specific ODH rate for the $1\text{Pt}_{0.2}\text{Ir}_{0.8}/\text{MgAl}_2\text{O}_4\text{-FR}_{2\text{h}}$ is slightly higher than that for the monometallic $1\text{Pt}/\text{MgAl}_2\text{O}_4\text{-FR}_{2\text{h}}$ catalyst, indicating a possible promoting effect by mixing Pt with Ir. However, it is still not clear whether the enhancement is due to electronic or geometric effects. Thus we

further evaluated the Pt mass specific ODH rates for catalysts with various total Pt-Ir loadings (2 - 10 wt.%) but same Pt to Ir atomic ratio (1:4), which are supposed to have similar mixing patterns of Pt and Ir. The methanol ODH rate monotonically decreases from 13.1 to 10.2, 7.0 and to 4.7 mol/mol_{Pt-total}·S⁻¹ with the total PM loading increasing from 2 to 3, 5 and to 10 wt.%, respectively (Figure S3). These results suggest that the metal loading related parameters like particle sizes (Figure S4) or metal dispersions affect the Pt mass specific ODH rates more significantly. On the other hand, Pt-Ir bimetallic catalysts give similar products to the Pt catalysts; and the selectivities are very similar especially on aged catalysts in which all the small bi- and monometallic particles are all on MgAl₂O₄ spinel {111} facets (Table S1). Thus the electronic effects of Ir mixing with Pt on the methanol ODH rate should not be much if present at all. It is reasonable to assign the catalytic activity totally to surface Pt atoms, whose enhancement indicates an increase in the number of exposed surface Pt atoms. In other words, the addition of Ir just helped increase the amount of Pt atoms exposed.

Figure 5. Simplified cross sectional schematics of possible evolutions of Pt-Ir nano-alloy particle during cyclic thermal treatments in oxidizing and reducing atmospheres. The Pt atoms are in magenda and the Ir atoms are in blue.

Generally, bimetallic alloy particles tend to reconstruct to a lowest surface energy structure upon oxidizing and reducing thermal treatments. In this study, the small bimetallic particles in the 1Pt_{0.2}Ir_{0.8}/MgAl₂O₄-FR_{2h} undergo two different transformations during aging: those on MgAl₂O₄ spinel {111} facets remain stable as small bimetallic particles; the metal particles over the MgAl₂O₄ spinel {100} facets sinter to large Pt and Ir particles. These results demonstrate dramatic influence of the support to the stabilization of precious metal particles. Such strong influence makes the small metal particles exhibiting properties far different from their bulk properties. For example, the surface energy of Pt (111) becomes larger than that of Pt (100) [12,13]. For the stable small metal particles, the numbers of surface Pt increase after long-term oxidizing and short-term reducing but decrease after further prolonging reducing treatment as probed by methanol ODH reaction. Since in this contribution, all the samples were reduced by hydrogen, we first address the possible structural changes for metallic particles on spinel surface. Several factors, such as cohesive energy, surface energy, and metal-support interfacial energy and interaction, can affect the structure and the thermal stability. Accordingly, as illustrated in Figure 5, there are at least three typical processes that can lead to changes in surface compositions: a). if the Pt-Ir cohesive energy is much smaller than their respective ones [20,21], bimetallic alloy can undergo phase segregation readily to form monometallic small particles on the MgAl₂O₄ spinel (111) surface which is difficult to re-alloy and

form solid solution. However, such evolutions won't change the ratio of Pt atoms on surface to in bulk; b). With the lower surface energies of Pt than Ir [20,21], surface segregation can happen and Pt enriches on the surface. However, this monotonic surface Pt enriching process cannot explain the detected decrease in surface Pt with prolonging the reduction periods. Hence, these two types of processes involving relative migrations of Pt and Ir atoms within a bimetal particle cannot explain the detected changes in surface Pt atoms. c). with the strong metal-support interaction, reversible migrations of metal species between metal particles and support surface may happen. Comparing to Pt, Ir is more oxyphilic so that Ir can more readily wet the spinel surface during oxidizing aging, leaving relative more Pt on the particle surface. On the other hand, after reducing, the oxides are reduced into metallic species, partially weakening the interactions. Together with the high metal cohesive energy [20,21], metallic iridium species re-nucleate on the Pt enriched particle surface, reducing the surface Pt atoms. Such a dynamic migration of surface atoms can well explain the detected variations of surface Pt atoms during cyclic oxidizing and reducing thermal treatments. In addition, based on the general phenomena that the 1Pt_{0.2}Ir_{0.8}/MgAl₂O₄-1WR_{2h} presents more single atomic species surrounded metal particles than the 1Pt_{0.2}Ir_{0.8}/MgAl₂O₄-FR_{2h}, this wetting-nucleation dynamic process is reasonably proposed.

In summary, we have successfully stabilized small Pt-Ir bimetallic nano-alloy particles on MgAl₂O₄ spinel {111} facets. In particular, the number of surface Pt atoms, probed by methanol oxidation dehydrogenation (ODH) reaction, increases with long-term oxidizing and short-term reducing but decreases with further prolonged reduction. A dynamic stabilization mechanism involving wetting/nucleation processes during oxidizing/reducing cyclic thermal treatments can well explain the exceptional surface reconstructions. Such significant enhancement in the utilization efficiency of costly Pt, especially at oxidizing atmospheres, provides a viable way for developing practical catalysts for catalytic oxidation reactions at high temperatures.

ASSOCIATED CONTENT

Supporting Information

Methods and additional data. This material is available free of charge via the Internet at Elsevier.

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Notes

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Table of Contents artwork