# Size Limit of Support Particles in an Oxide-Supported Metal Catalyst: Nanocomposite Ni/ZrO<sub>2</sub> for Utilization of Natural Gas

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This paper explores the size effect of zirconia particles on the catalysis of Ni metal for  $CO_2$  re-forming of methane. It is revealed for the first time that when the sizes of zirconia particles become samller than 25 nm, the oxide forms nanocomposite catalysts with size-comparable Ni-metal nanocrystals (10–15 nm). The nanocomposite catalysts show extremely stable catalysis, which is in strong contrast with the deactivating Ni catalyst supported on bigger zirconia particles (>25 nm). This raises the possibility of tailoring the catalytic behavior of oxide-supported metal catalysts by reducing the particle size of oxide to make high-performance nanocomposite catalysts.

### 1. Introduction

Oxide-supported metal catalysts are a very important class of industrial catalysts that are closely related with many key technologies in chemical/petrochemical industries, in environmental protection, in chemical sensors, and in the manufacture of fine and special chemicals.<sup>1</sup> Often in this kind of catalyst system, discrete metal nanocrystals (typically 1-15 nm) are dispersed on support particles that are one to several orders of magnitude larger than the supported metal nanoparticles. The most important function of a support is to provide proper texture/ pore structure and high surface area to disperse and maintain the active metal catalyst.<sup>2</sup> Structure-sensitive or -insensitive concepts are developed to describe the observations that catalysis of metal catalyst is dependent or independent of the size of the metallic nanocrystals.<sup>3</sup> When the particle sizes of an oxide support are reduced to such an extent that they become comparable to that of the active metal particles, the oxide may deviate dramatically from its function as a conventional catalyst support. Such metal/oxide catalyst with size-comparable metal and oxide nanocrystals may be better called a metal/oxide nanocomposite rather than an "oxide-supported" metal catalyst.<sup>4</sup> But it is unknown whether there is a lower limit to the particle size of an oxide support for the so-called oxide-supported metal catalysts. Here, we investigate the size effect of zirconia nanocrystals on the catalysis of Ni metal for CO<sub>2</sub> re-forming of methane. We find that nanocomposites of size comparable to Ni metal (10-15 nm) and zirconia (7-25 nm) show extremely stable catalysis whereas Ni catalyst supported on bigger zirconia particles (>25 nm) deactivates very rapidly. This raises the possibility of tailoring the catalytic behavior of oxidesupported metal catalysts by reducing the particle size of oxide to make metal/oxide nanocomposite catalysts.

 $CO_2$  re-forming of methane over heterogeneous catalysts to produce a syngas with equal moles of CO and H<sub>2</sub> is one of the attractive routes for the utilization of the methane and  $CO_2$ resources.<sup>4–8</sup> Some natural gas reservoirs contain, in addition to methane, also a large fraction of CO2. Moreover, the use of CO<sub>2</sub> provides a clean and cheaper oxygen source for the reaction, which eliminates the costly separation processes required for partial oxidation of methane. This reaction is also considered for energy transformation or chemical heat-pipe applications.<sup>6–8</sup> Ni-based catalysts possess high initial activity for the reaction but suffer from a rapid deactivation due to carbon deposition, which hinders the process from industrial applications.<sup>4,5</sup> In earlier work, we demonstrated<sup>9-11</sup> that the use of nano-ZrO<sub>2</sub> particles (15-20 nm) as "support" for nickel catalyst led to extremely stable Ni/ZrO<sub>2</sub> catalysts that are highly active for the CO<sub>2</sub>/CH<sub>4</sub> reaction. We have discovered that a change of the conventional hydrogels of metal hydroxides to their alcogels followed by nanocrystal formation under controlled atmospheres at elevated temperature can lead to size control synthesis of nanocrystals of zirconia<sup>12</sup> and other oxides.<sup>13,14</sup> This discovery makes it possible to address the particle size effect of ZrO<sub>2</sub> "support" on the performance of Ni catalyst by reducing the particle size of ZrO<sub>2</sub> down to the extent that it becomes indistinguishable from particles of the metal catalyst.

#### 2. Experimental Section

2.1. Preparation and Catalytic Testing of Ni/ZrO<sub>2</sub> Catalyst. Following our previous sample coding,<sup>4,13</sup> ZrO<sub>2</sub>-AS is the sample prepared by drying under supercritical ethanol (270 °C, 7.0 MPa) of an ZrO(OH)<sub>2</sub> alcogel, which was obtained by washing a conventional ZrO(OH)<sub>2</sub> hydrogel with anhydrous ethanol. A processing of the alcogel at 270 °C in flowing nitrogen under normal pressure gave sample ZrO<sub>2</sub>-AN. And, the digesting of the same alcogel in anhydrous ethanol under reflux (78–80 °C) and then processing at 270 °C in flowing nitrogen produced the ZrO<sub>2</sub>-AD sample. The later physical characterizations (XRD, TEM, BET, etc.) of these alcogel-derived ZrO<sub>2</sub> made use of the samples further calcined at 650 °C for 5 h in flowing air. The ZrO<sub>2</sub>-CP and -CN samples were prepared respectively by conventional calcination at 650 °C of the ZrO(OH)<sub>2</sub> hydrogel in flowing air and nitrogen.

 $Ni/ZrO_2$  catalysts were obtained by impregnation of aqueous  $Ni(NO_3)_2$  onto the oxide precursors dried at 270 °C with a rotary evaporator. Details for the catalyst preparation were described

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earlier.<sup>10,11,13</sup> The loading of nickel was kept between 12% and 13% by the weight and was checked out with XRF analysis. Earlier data from this lab have revealed that this amount of Ni loading seems to be an optimum for Ni/ZrO<sub>2</sub> catalyst.<sup>4,11</sup> After drying at 110 °C, the samples were calcined in air at 650 °C for 5 h, and then stored for further use. Our preparations and catalytic tests, to be reported elsewhere,<sup>15</sup> show that the behavior of the alcogel-derived Ni/ZrO<sub>2</sub> catalysts in methane re-forming reaction by CO<sub>2</sub> is basically not affected by the precalcination temperature (270–650 °C) of the ZrO(OH)<sub>2</sub> alcogel in nitrogen, where precalcination means processing at the elevated temperatures before the impregnation of the nickel salt.

The catalytic reaction was conducted at 757 °C in a vertical fixed-bed U-shape quartz reactor (i.d. 10 mm) under atmospheric pressure, as described previously.<sup>4,11,13</sup> The reaction temperature was measured by a thermal couple in a quartz-well inserted into the catalyst bed. Unless otherwise specified, the flow rate of the feed, a 1:1 (molar) mixture of methane and CO<sub>2</sub> without using any inert diluent gas, was GHSV =  $2.4 \times 10^4$  to  $3.8 \times 10^5$  mL/(h·g of cat). Before the reaction, the catalyst was reduced in situ with a flow of 10% H<sub>2</sub>/N<sub>2</sub> at 700 °C for 3 h.

**2.2. Sample Characterizations.** The crystal structure of  $ZrO_2$  and Ni/ZrO<sub>2</sub> samples were characterized with powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer using the Cu K2 $\alpha$  source at 40 kV and 40 mA. The percentage of monoclinic phase (M%) of the oxide solids was measured according to the equation of Srinivasan et al.:<sup>16</sup>

$$\mathbf{M}\% = I_{\mathbf{M}(\bar{1}11)} / (1.6I_{\mathbf{M}(\bar{1}11)} + I_{\mathbf{T}(111)})$$

where  $I_{M(\bar{1}11)}$  and  $I_{T(111)}$  are the diffraction intensities of the monoclinic (111) and tetragonal (111) planes, respectively. The average size of ZrO<sub>2</sub> crystals was measured with the X-ray broadening analysis (XLBA) by using the well-known Scherrer equation:<sup>17</sup>

$$d = 0.089\lambda/(B(2\theta)\cos\theta)$$

where  $B(2\theta)$  is the width of the XRD pattern line at half peak height in radians,  $\lambda$  is the wavelength of the X-ray,  $\theta$  is the angle between the incident and diffracted beams in degrees, and *d* is the crystal size of the powder sample in nanometers.

Surface areas of the samples were measured with nitrogen adsorption at -196 °C on a Micromeritics ASAP 2010C instrument. The samples were dehydrated with flowing dry nitrogen at 200 °C for 5 h before the adsorption measurement. TEM measurements of some samples were performed on a Hitachi H-800 electron microscope to check the crystal sizes of Ni and ZrO<sub>2</sub>.

Quantitative TPR measurement was done on a homemade temperature-programmed analysis system with a temperature ramp of 15 K/min with procedures similar to those reported in refs 13 and 18. The TPR measurement was followed by an H<sub>2</sub>-TPD to measure the chemisorption of hydrogen. The ratio of 2 × (area of the TPD peak)/(area of the TPR peak) gives the dispersion (*D*) of the reduced nickel metal, whereas the inverse of the dispersion data, 1/*D*, provides an estimation of the crystal size of the nickel metal catalyst.<sup>13,17</sup>

## 3. Results and Discussion

After calcination in air at 650 °C, the alcogel derived  $ZrO_2$ -AD, -AS, and -AN samples exist as mixtures of the monoclinic (M) and tetragonal (T) phases. The phase composition and XLBA sizes of the monoclinic and tetragonal crystals together with the TEM particle sizes are given in Table 1. It is apparent

TABLE 1: Physicochemical Properties of  $ZrO_2$  after Calcination at 650  $^\circ\text{C}$ 

sample	BET surface (m <sup>2</sup> /g)	ZrO <sub>2</sub> phase <sup>a</sup> (%)	XLBA size <sup>b</sup> (nm)	TEM size <sup>c</sup> (nm)
ZrO <sub>2</sub> -AD	85	M45/T55	M9.9/T10.0	$7-12 \\ 15-20 \\ 18-25 \\ 30-60 \\ 40-200$
ZrO <sub>2</sub> -AS	44	M30/T70	M15.1/T15.4	
ZrO <sub>2</sub> -AN	43	M64/T36	M20.8/T20.2	
ZrO <sub>2</sub> -CN	28	M80/T20	M23.8/T20.6	
ZrO <sub>2</sub> -CP	26	M98/T2	M22.5	

<sup>*a*</sup> M and T represent monoclinic and tetragonal phases, respectively. <sup>*b*</sup> Average crystal size obtained with the Scherrer equation by using the (111) diffraction  $(2\theta = 28.5^{\circ})$  for monoclinic and the (111) diffraction  $(2\theta = 30.4^{\circ})$  for tetragonal crystals, respectively. <sup>*c*</sup> Particle size measured by TEM.

that the XLBA sizes of tetragonal crystals are very close to the sizes of the monoclinic ones in the alcogel-derived samples, which seems at variance with conventional opinion that the tetragonal crystal should be significantly smaller than the monoclinic at the temperature used, but the discussion of the crystal sizes of the two phases is beyond the scope of this work. The agreement in particle sizes from XLBA and TEM measurements for the ZrO<sub>2</sub>-AD (XLBA, 10 nm; TEM, 7–12 nm), -AS (XLBA, 15–16 nm; TEM, 15–20 nm), and -AN (XLBA, 20–21 nm; TEM, 18–25 nm) samples indicates that the alcogel-derived ZrO<sub>2</sub>-AD, -AS, and -AN samples are composed of discrete nanocrystals with sizes less than 25 nm.

The ZrO<sub>2</sub>-CP and ZrO<sub>2</sub>-CN samples contain ZrO<sub>2</sub> nanocystals averaged respectively to 20-24 and 22.5 nm by XLBA; however, TEM data show that the nanocrystals form larger hard aggregates of 30-60 nm in ZrO<sub>2</sub>-CN and 40-200 nm in ZrO<sub>2</sub>-CP samples. The surface area data (ZrO<sub>2</sub>-AD, 85 m<sup>2</sup>/g; ZrO<sub>2</sub>-AS, 44 m<sup>2</sup>/g; ZrO<sub>2</sub>-AN, 43 m<sup>2</sup>/g; ZrO<sub>2</sub>-CN, 28 m<sup>2</sup>/g; ZrO<sub>2</sub>-CP, 26 m<sup>2</sup>/g) are closely related to the sizes of zirconia particles, also confirming that the conventionally prepared samples (ZrO<sub>2</sub>-CP and -CN) were present as hard aggregates of sintered nanocrystals.

The physicochemical properties of the reduced Ni/ZrO2 catalysts are presented in Table 2. The XRD measurements (Figure 1) showed no evidence for any possible compound formation between nickel and zirconia in the samples. The loaded nickel ions were found completely reducible, as indicated by the reducibility data in Table 2, in the temperatureprogrammed reduction (TPR) with hydrogen. It is important to note that the particle sizes of Ni metal estimated from the Nidispersion data for the Ni/ZrO2-AD, -AS, and -AN samples were comparable to the sizes of zirconia "support" in the same samples as shown in the last two columns of Table 2. This information was further confirmed by TEM micrograms of the reduced Ni/ZrO<sub>2</sub> catalysts in Figure 2. Energy dispersive analysis of X-rays (EDAX) showed that the majority of the dark particles in the TEM micrograms were images of the Ni-metal crystals whereas particles in lower contrasts were most likely crystals of zirconia. A further selected area EDAX probe detected no evidence of any significant contamination between the metal and oxide components. Thus, these catalysts (Ni/ZrO<sub>2</sub>-AD, -AS, and -AN) can better be called nanocomposites of sizecomparable Ni-metal and zirconia nanocrystals. High-resolution TEM measurements coupled with EDAX and electron diffraction analysis confirmed the nanocomposite nature by showing that the nanosize (10-15 nm) Ni-metal crystals were surrounded by zirconia nanocystals of 15-25 nm, as shown in Figure 3 with Ni/ZrO<sub>2</sub>-AS as an example. On the other hand, the metal particles in Ni/ZrO<sub>2</sub>-CP and -CN samples, which used big particles of zirconia (>30 nm) as the support, were much smaller

TABLE 2: Physicochemical Properties of Ni/ZrO<sub>2</sub> Catalysts After the Reduction at 700 °C

sample	Ni load <sup>a</sup> (wt %)	BET surface (m <sup>2</sup> /g)	Ni red <sup>b</sup> (Ni %)	$ZrO_2 phase^c$ (%)	Ni disp <sup>d</sup> (%)	Ni size <sup>e</sup> (nm)	ZrO <sub>2</sub> size <sup>f</sup> (nm)
Ni/ZrO <sub>2</sub> -AD	12.6	62	98.6	M51/T49	11.1	9.1	7-12
Ni/ZrO <sub>2</sub> -AS	12.5	35	109.1	M45/T55	9.0	11.1	15-20
Ni/ZrO <sub>2</sub> -AN	12.1	38	95.2	M41/T59	9.4	10.6	18-25
Ni/ZrO <sub>2</sub> -CN	12.7	29	93.5	M35/T65	5.6	17.2	30-60
Ni/ZrO <sub>2</sub> -CP	12.9	18	98.5	M5/T95	5.8	17.8	40-200

<sup>a</sup> Measured from X-ray fluoroscence analysis. <sup>b</sup> Reducibility of nickel measured from temperature-programmed reduction (TPR) with 5% H<sub>2</sub>/Ar, as described in ref 13. <sup>c</sup> M and T represent monoclinic and tetragonal phases, respectively. <sup>d</sup> Dispersion of nickel obtained from temperatureprogrammed desorption (TPD) of hydrogen after the TPR measurement.  $^{e}$  Particle size of Ni metal (d) calculated with the assumption: d = 1/d is persion. <sup>f</sup> Particle size of zirconia measured by TEM.



Figure 1. X-ray diffraction patterns of Ni/ZrO2 catalysts after reduction at 700 °C.





## Ni/ZrO<sub>2</sub>-AN

# Ni/ZrO<sub>2</sub>-CP

Figure 2. TEM micrograms of the reduced Ni/ZrO<sub>2</sub> catalysts. Electron diffraction pattern analysis (not shown here) reveals that the samples are mixtures of metallic nickel and zirconia crystals.

than the support particle; these two samples could be regarded as conventional zirconia-supported nickel catalysts.

The catalytic data of the methane re-forming reaction at 757 °C with GHSV of the reactants at 2.4  $\times$  10<sup>4</sup> mL/(h·g of cat) are given in Figure 4 by plotting CH<sub>4</sub> conversion against the



Figure 3. High-resolution TEM microgram of the reduced Ni/ZrO2-AS catalyst, showing that the Ni-metal nanocrystal is surrounded by size-comparable crystals of zirconia. Energy dispersive analysis of X-rays focused on individual particles showed little contamination between Ni-metal and zirconia nanocrystals.



Figure 4. Catalytic activity by methane conversion and stability of Ni/ZrO<sub>2</sub> catalysts at 757 °C. Note: the particle sizes of ZrO<sub>2</sub>-AD, -AS, -AN, -CN, and -CP are 7-10, 15-20, 20-25, 30-60, and 40-200 nm, respectively.

reaction time-on-stream over the different Ni/ZrO<sub>2</sub> catalysts; similar curves were obtained for the CO<sub>2</sub>-conversion data. The selectivity of syngas in the products was higher than 97% with a CO/H<sub>2</sub> molar ratio of ca. 1.2, and this ratio did not change during the long lasting reaction. Quantitative analysis of product H<sub>2</sub>O confirms, as in our earlier reports,<sup>4,10,11</sup> that the deviation from the theoretical product ratio (CO/H<sub>2</sub> = 1.0) is due to an occurrence of the unavoidable reverse water-gas shift reaction. Although Ni/ZrO<sub>2</sub>-CP and -CN catalysts exhibited high activities that conversions of the reactants were close to their equilibrium values (86%-90%) under the conditions used, rapid deactivation of these two catalysts was apparent in less than 50 h. Rapid deactivation of conventionally prepared Ni/ZrO2 catalyst was also reported in earlier literature.<sup>19</sup> In contrast, the nanocomposite Ni/ZrO<sub>2</sub>-AS, -AN, and -AD catalysts showed very stable



**Figure 5.** Catalytic activity by methane conversion and stability of Ni/ZrO<sub>2</sub>-AS catalysts at 757 °C at different space velocities of the reactants: GHSV = 24 000 (A), 48 000 (B), 72 000 (C), 96 000 (D), 192 000 (E), 240 000 (F), 288 000 (G), 336 000 (H), and 384 000 mL/ (h·g of cat.) (I).

catalytic activities for the re-forming reaction in 100–250 h. Previously, we reported<sup>4,10,11</sup> that the catalysis of a 27%Ni/ZrO<sub>2</sub>-AS (denoted as 27%Ni/ZrO<sub>2</sub>-B in the original publication) catalyst is stable for more than 600 h.

The Ni/ZrO<sub>2</sub>-AD catalyst was further tested for 500 h in the present study, and we detected no catalyst deactivation. Another catalytic test up to 1100 h with the Ni/ZrO<sub>2</sub>-AN catalyst also showed no deactivation during the entire reaction period.<sup>20</sup> To demonstrate the catalyst stability at methane and CO<sub>2</sub> conversions far below their thermodynamic equilibrium values (86%-90%), the present Ni/ZrO2-AS catalyst was tested with stepwise increasing of the space velocity by 15-fold up to GHSV = 3.8 $\times$  10<sup>5</sup> mL/(h·g of cat), and the results are given in Figure 5. The observed catalytic methane and CO<sub>2</sub> (not shown in the figure) conversions were stable every time after changing the reaction GHSV. And, surprisingly, the conversion at every specific GHSV was kept constant after switching between many different GHSVs during 550 h reaction time-on-stream. Other tests on the deactivating Ni/ZrO2-CP and -CN catalysts with  $GHSV = 2.4 \times 10^5 \text{ mL/(h \cdot g of cat)}$  showed that they deactivate much more rapidly than they were reacted in Figure 4 with the 10-fold lower GHSV. These results further demonstrated the extremely stable catalysis of the nanocomposite Ni/ZrO<sub>2</sub>-AD, -AS, and -AN catalysts. TEM measurements of the used stable catalysts showed that the particle sizes of both the Ni-metal and zirconia crystals were virtually maintained when the flow of CO<sub>2</sub> was used to cool the catalyst.

It is well-known that ZrO<sub>2</sub> crystallizes in two different phases: tetragonal and monoclinic. The phase composition of the zirconia support in the reduced catalysts is characterized by XRD (Figure 1 and Table 2). Although the transformation of the tetragonal to monoclinic phase was inhibited in the support of the deactivating Ni/ZrO<sub>2</sub>-CP catalyst, the very similar phase composition of the support between the stable alcogel derived Ni/ZrO<sub>2</sub>-AN and the deactivating Ni/ZrO<sub>2</sub>-CN reveals that the difference in phase composition of the support seems not a cause of the difference in catalyst stability in Figure 4.

It is shown that the there are no significant differences in sizes of tetragonal and monoclinic nanocrystals in the present support oxides (Table 1). The catalytic performances of Ni catalysts on the ZrO<sub>2</sub>-AD (7–10 nm), -AS (15–20 nm), -AN (18–25 nm), -CN (30–60 nm), and -CP (40–200 nm) in Figure 4 thus can be explained with a particle size effect of the zirconia "support". For stable Ni catalyst, it seems crucial to keep the ZrO<sub>2</sub> particles as discrete crystals with sizes less than 25 nm. This is thus an up-limit of zirconia particle for obtaining the stable Ni catalysts in the high-temperature CO<sub>2</sub>/CH<sub>4</sub> reaction. Our very recent investigation into the effect of processing temperature of ZrO(OH)<sub>2</sub> alcogel, before the loading of nickel,



Figure 6. Effect of Ni loading on the catalytic activity and stability of Ni/ZrO<sub>2</sub>-AS catalyst at 757 °C. Reaction conditions are the same as for Figure 4.



Figure 7. X-ray diffraction patterns of reduced Ni/ZrO<sub>2</sub>-AS catalysts with different nickel loadings.

on the preparation of Ni/ZrO<sub>2</sub> also indicates that nanozirconia crystals in stable Ni/ZrO<sub>2</sub>-AN catalysts can be mainly either tetragonal or monoclinic, providing that the sizes of the crystals are not bigger than 25 nm.<sup>15</sup> To our knowledge, this is the first example to show a size limit of nano-oxide particles for a metal catalyst. We believe that the oxide particles in these stable Ni/ZrO<sub>2</sub> catalysts can no longer be named as a support for the crystals of Ni metal because these particles are not capable of holding/supporting a number of the metal crystals (refer to Figures 2 and 3).

We further investigated the effect of nickel loading in the *nanocomposite* Ni/ZrO<sub>2</sub>-AS catalyst.<sup>4,10,11</sup> It appears that the catalytic stability seems not affected in the range of 5–27% nickel loading (Figure 6). The sizes of Ni catalysts measured by hydrogen adsorption and TEM in these samples are in the range between 5.5 nm in 5% Ni/ZrO<sub>2</sub> and 16.5 nm in 27% Ni/ZrO<sub>2</sub>. Again, the crystal phase composition of the support oxide, which contains 45%, 55%, and 65% tetragonal phase in the 5%, 12%, and 27%Ni/ZrO<sub>2</sub> catalysts, respectively (Figure 7), did not affect significantly the catalyst stability. Reduction of the particle sizes of MgO and Al<sub>2</sub>O<sub>3</sub> has also led to stable Ni/MgO<sup>13</sup> and Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub><sup>14</sup> catalysts, which implies that the metal/oxide *nanocomposite* concept could be applicable to other metal/oxide catalysts.

The question why nanocomposite Ni/ZrO<sub>2</sub> catalysts become so stable remains to be answered in future research. It is generally agreed that the long-term activity of the catalyst in the re-forming reaction is dependent upon the balance between the rate of CH<sub>4</sub> decomposition and the rate of CO<sub>2</sub> dissociation. CH<sub>4</sub> decomposition to give hydrogen occurs easily on the Nimetal catalyst; the carbon atoms left from this reaction remain on the metal surface. Oxidative removal of the carbon atoms to produce CO requires a transfer of surface oxygen atoms from either a reduction of the oxide or from CO<sub>2</sub> activation at the metal/oxide *boundary* or *perimeter*.<sup>10,19,21–24</sup> It is believed that the oxygen transfer ability was significantly enhanced by reducing the particle size of zirconia to less than 25 nm or by the formation of metal/oxide *nanocomposites*. This is not a surprise because a much higher percentage of *metal/oxide boundaries or perimeters* exists in the nanocomposite system.

The present data raise a general issue that a lower limit in the nanometer range may exist for the size of oxide support particles in supported metal catalysts. When sizes of the support particles become further smaller, the metal/oxide catalyst forms *nanocomposites* that could show distinctive catalytic performances. This may have important implication on the design and preparation of advanced metal catalysts for many key technologies.

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