Accepted Manuscript

Title: Oxidative Coupling of Methane (OCM): Effect of Noble Metal (M = Pt, Ir, Rh) Doping on the Performance of Mesoporous Silica MCF-17 Supported Mn_xO_y -Na₂WO₄ Catalysts



Authors: Wen-Chi Liu, Walter T. Ralston, Gérôme Melaet, Gabor A. Somorjai

PII:	S0926-860X(17)30317-4
DOI:	http://dx.doi.org/doi:10.1016/j.apcata.2017.07.017
Reference:	APCATA 16322
To appear in:	Applied Catalysis A: General
Received date:	27-4-2017
Revised date:	23-6-2017
Accepted date:	12-7-2017

Please cite this article as: Wen-Chi Liu, Walter T.Ralston, Gérôme Melaet, Gabor A.Somorjai, Oxidative Coupling of Methane (OCM): Effect of Noble Metal (M = Pt, Ir, Rh) Doping on the Performance of Mesoporous Silica MCF-17 Supported MnxOy-Na2WO4 Catalysts, Applied Catalysis A, Generalhttp://dx.doi.org/10.1016/j.apcata.2017.07.017

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Oxidative Coupling of Methane (OCM): Effect of Noble Metal (M = Pt, Ir, Rh) Doping on the Performance of Mesoporous Silica MCF-17 Supported Mn_xO_y-Na₂WO₄ Catalysts

Wen-Chi Liu^{†,‡}, Walter T. Ralston^{†,§}, Gérôme Melaet^{†,‡}, Gabor A. Somorjai^{*,†,‡}

[†]Department of Chemistry, University of California, Berkeley, California 94720, United States [‡]Materials Sciences Division and [§]Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Graphical abstract



Highlights

- $M-Mn_xO_y-Na_2WO_4$ (M = Pt, Ir, Rh) catalysts were prepared on mesoporous silica MCF-17.
- Enhanced C_2 selectivity in OCM was obtained in the order of Rh > Ir > Pt-doped catalysts.
- Reducibility of W and Mn species was modified by noble metal additives
- Optimized strength of interaction between the surface and intermediates was suggested.

Abstract

Noble metal doped M-Mn_xO_y-Na₂WO₄/SiO₂ (M = Pt, Ir, Rh) catalysts were prepared via a wet impregnation method using mesoporous silica MCF-17 as support, and their performance in the oxidative coupling of methane (OCM) was studied in a fixed-bed flow reactor. The reaction was carried out at 750 °C under atmospheric pressure with a gas feed composition of CH₄:O₂ = 4:1. The incorporation of the noble metals yielded an enhanced selectivity towards both C₂ and C₃ hydrocarbons as compared to the undoped Mn_xO_y-Na₂WO₄/MCF-17 catalyst in the order of Rh-doped > Ir-doped > Pt-doped samples together with a lower olefin to paraffin ratio. On the other hand, the Ir-doped catalyst showed the highest overall yield

for C_2 production. Elemental analysis, N₂-adsorption, and X-ray powder diffraction (XRD) measurements confirmed similar metal loading, surface area, and phase composition for both the undoped and doped catalysts. Electron microscopy analysis showed a near-homogeneous distribution of Na and W but a higher tendency to form aggregates for Mn, with the Rh-doped catalyst being the best in overall elemental dispersion. X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (H₂-TPR) results indicate a more reduced nature of the surface oxide species in the noble metal doped catalysts as compared to the undoped one. They also suggest a more optimized strength of interaction between the carbon intermediates and the surface of the noble metal doped catalysts, which in combination with the improved reducibility of Mn and W species and metal dispersion, accounted for the enhanced C₂ production on the noble metal doped Mn_xO_y-Na₂WO₄/MCF-17 catalysts.

Keywords: Oxidative coupling of methane; Mn_xO_y-Na₂WO₄/SiO₂; Noble metal additives; C₂ production;

1. Introduction

Oxidative coupling of methane, in which CH₄ molecules are catalytically transformed into C₂ hydrocarbons in the presence of an oxidizing reagent, possesses the potential capability of directly utilizing natural gas for the production of value added chemicals. [1–4] Different types of catalysts and combinations thereof have been examined for this reaction, and the Mn_xO_y-Na₂WO₄/SiO₂ system is among the very few of those that provide high C₂ yield and excellent stability at the same time. [5,6] Extensive research has been performed on this catalyst system, in which the effect of the preparation methods, elemental concentrations, and the variation of each of its components have been reported. [7] For catalyst preparation, the wet impregnation and the mixture slurry methods are proven to be more efficient in producing high-performance catalysts. [8] As for the catalyst composition, results have indicated that there exist a range of combinations, i.e., 0.4–2.3% for Na, 2.2–8.9% for W, and 0.5–3.0% for Mn, that would allow an optimized C₂ yield. [9] In addition, Yildiz et al. showed that by simply utilizing a mesoporous silica support, the elemental dispersion is improved, resulting in a higher overall C₂ production. [10,11]

In spite of the large amount of work performed on this catalytic system in the OCM reaction, the effect of noble metal additives is experimentally less explored. In liquid phase homogenous catalysis, noble metal complexes including that of Pt, Rh, and Ir are widely used as catalysts for C-H bond activation. [12,13] In addition, there have been several theoretical investigations suggesting a potential promotional

effect on the CH₄ activation and C-C bond coupling on the surface of IrO₂. [14–16] Therefore, it is reasonable to explore the effect of noble metal doping on the performance of the $Mn_xO_y-Na_2WO_4/SiO_2$ system.

Herein, we report the investigation on the effect of noble metal doping (M = Pt, Ir, Rh) on the performance of the $Mn_xO_y-Na_2WO_4/SiO_2$ system. The catalysts were synthesized via a wet impregnation method with mesoporous silica material MCF-17 as the support. Their structural and chemical properties were characterized using techniques including X-ray powder diffraction (XRD), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM)/energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM), inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray photoelectron spectroscopy (XPS), N₂-adsorption, and H₂-TPR. The catalytic performance of the M-Mn_xO_y-Na₂WO₄/SiO₂ system (M = Pt, Ir, Rh) was studied in a continuous flow reactor, of which the results are compared and discussed in combination with the information obtained from the characterization studies.

2. Experimental

2.1. Preparation of Mn_xO_y-Na₂WO₄/MCF-17 catalysts

The mesoporous silica material MCF-17 was prepared beforehand using a method reported previously. [17] It has cell-like mesopores with tunable sizes that are connected by windows, large surface area and pore volume, and has been used as the catalyst support in various applications, such as Fischer-Tropsch synthesis and alkane isomerization reactions. [18–20] In a typical synthesis, a desired amount of MCF-17 was firstly impregnated with an aqueous solution of manganese (II) acetate (Sigma-Aldrich, \geq 99 %) at room temperature and then dried in air at 80 °C overnight. Afterwards, the mixture was impregnated with an aqueous solution of sodium tungstate (Sigma-Aldrich, \geq 99 %) at room temperature followed by drying in air at 80 °C overnight. The obtained material was calcined in air at 750 °C for 1 h with a heating rate of 1 °C/min. The obtained catalyst is denoted as 'Original'.

2.2. Preparation of M-Mn_xO_y-Na₂WO₄/MCF-17 (M = Pt, Ir, Rh) catalysts

The preparation of noble metal doped $Mn_xO_y-Na_2WO_4/MCF-17$ catalysts follows a similar procedure described above. After impregnation with manganese (II) acetate and sodium tungstate and dried at 80 °C overnight, the obtained material was then divided into three portions with each being impregnated with a certain metal precursor (Sigma-Aldrich, rhodium(III) acetylacetonate [Rh(acac)_3, 97%], platinum(II) acetylacetonate [Pt(acac)_2, 97%], or Iridium(III) acetylacetonate [Ir(acac)_2, 97%]) dissolved in chloroform [Fisher Scientific, \geq 99%]. The calcination process was carried out in air at 750 °C for 1 h with a heating

rate of 1 °C/min. The obtained catalysts are denoted as 'Pt-doped' for M = Pt, 'Ir-doped' for M = Ir, and 'Rh-doped' for M = Rh.

2.3. Characterizations of M-Mn_xO_y-Na₂WO₄/MCF-17 (M = Pt, Ir, Rh) catalysts

XRD measurements of the fresh and spent catalysts were performed using a Bruker D2 Phaser Benchtop X-ray powder diffractometer with a Cu x-ray source (K α 1.54184 Å). 2 theta value was varied from 10° to 60° with a step size of 0.02°.

TEM and STEM/EDS analysis were performed using a JEOL JEM2100F TEM equipped with an Inca Energy Dispersive Spectrometer operated at 200 kV. Samples for TEM analysis were prepared by first dispersing the catalysts in ethanol and then dropping the dispersion on ultrathin lacey carbon TEM grids (Ted Pella, Inc.).

SEM images of the fresh catalysts were obtained with a FEI/Philips XL-30 Field Emission ESEM operated at 15 kV. Samples for SEM analysis were prepared by drop-casting the dispersion of the catalysts in isopropanol on a piece of silicon wafer.

The loading of the prepared catalysts was determined using ICP-AES on a PerkinElmer ICP Optima 7000 DV spectrometer. Samples for ICP-AES measurements were prepared by first digesting the catalysts powder with nitric acid and hydrofluoric acid and then diluting with deionized water.

The surface composition and oxidation states of the catalysts were examined using PHI 5400 XPS System with an Al X-ray source (Kα 1486.6 eV). A pass energy of 35.75 eV with a step size of 0.05 eV was used. Samples for XPS measurements were prepared by drop-casting the dispersion of the catalysts in isopropanol on a piece of silicon wafer. All samples were dried in a vacuum oven at 85 °C overnight before testing. The binding energies were corrected for charging effect with respect to the Si 2p line at 103.4 eV. [21,22] The spectra were fitted with a Shirley background and the area under the peaks is calibrated using the Relative Sensitivity Factor provided in the CasaXPS library.

The specific surface area and the pore structure of the catalysts were verified using N₂-adsorption at liquid nitrogen temperature on an ASAP 2020 Surface Area and Porosimetry System (Micromeritics). BET and BJH models were used for the determination of surface area and pore size distribution, respectively.

H₂-TPR measurements were carried out to assess the reducibility of the catalysts. A high purity mixture of 5% H₂/Ar (Praxair) flowing at 30 sccm was used as the reducing gas. The reactor was heated to 850 °C with a heating rate of ~6°C/min and the composition of the outlet gas was monitored by an online quadrupole mass spectrometer (SRS RGA 200).

2.4. Catalytic measurements

OCM reaction was performed in a home-built fixed bed flow reactor under atmospheric pressure. The catalysts were sieved to an average grain size of 150-250 um. Approximately 60 mg of the sieved catalyst was mixed with quartz sand (Umicore, 99.99%, grain size: 0.2-0.7 mm) and then packed in the center of a quartz reactor tube (Quartz Scientific, 16 inches, 4mm ID, 6.35mm OD) with quartz wool. Additional quartz sand was packed on both sides of the catalytic bed to help reduce the empty space of the reactor and promote heat dissipation. Methane (Praxair, 5.0 Research Grade) and synthetic air (Praxair, Ultra Zero) were fed into the reactor using carefully calibrated mass flow controllers (Parker) with a total flow rate of 60 sccm and a composition of $CH_4:O_2:N_2 = 4:1:4$. The reactor was heated to 750 °C with a heating rate of 8 °C/min by an electric tube furnace. Outlet gas was sampled and separated using an on-line GC-MS (Agilent 7890A-5975C) equipped with two capillary columns (HP-PLOT Q and HP-PLOT Mole-Sieve). The gaseous composition was analyzed by a thermal conductivity detector (TCD) and a flame ionization detector (FID) detector equipped with a methanizer. The equations used to determine the reaction conversion, selectivity, and carbon balance are provided in the supporting information.

3. Results and discussion

3.1. Characterizations

3.1.1. Surface area and porosity measurements

The BET surface area and pore structure of the MCF-17 support material and the supported catalysts are reported in Table 1. The pristine MCF-17 exhibits a surface area of 566 m²·g⁻¹, owing to its porous nature. The total pore volume is 1.6 cm³·g⁻¹ with an average pore size of 16 nm, which are typical among its category. After impregnation and calcination, the catalysts showed a significant loss of surface area and porosity (Table 1). The measured surface areas are among 7-9 m²/g and the total pore volumes are in the vicinity of 0.020 cm³·g⁻¹ for all the prepared catalysts. This could be explained by the structural change of the silica support induced by the phase transformation from amorphous SiO₂ to others forms, such as α -cristobalite and tridymite (Figure 2a), causing the collapse of the porous structure.

BET measurements of the spent samples were also performed and the measured surface area are typically around 4-5 m²/g for all the catalysts tested, indicating a slight decrease in the surface area after the reaction.

3.1.2. Composition analysis

The elemental compositions of the prepared catalysts as obtained from ICP-AES are shown in Table 2. The intended loading of each of the components were chosen to be within their optimal range, as mentioned in the introduction. It can be seen from Table 2 that the actual loading of the catalysts agrees well

with the theoretical values except for a slightly lower loading for W, yet there are no significant differences among the four catalysts. The determined loadings are 0.72 to 0.79 wt.% for Na, 2.29 to 2.51 wt.% for W, and 2.04 to 2.37 wt.% for Mn. ICP results also confirmed that Rh, Ir, and Pt are successfully incorporated into the catalysts, of which the metal loadings are in the vicinity of 0.12 wt.%.

3.1.3. TEM, SEM and STEM/EDS analysis

TEM and STEM measurements were performed to study the morphology and texture of the catalysts. The first column of Figure 1a-d shows the TEM images for the fresh catalysts, next to which their dark field (HAADF) images are also presented. The catalysts are generally in fibrous or rod-like shapes with small spherical and cubic aggregates distributed across the support. The SEM images (Figure S1) also indicate the existence of the particles on the surface of the catalysts. EDS point scans (Figure S2) revealed that the particles are mostly rich in Mn, with some of them also containing notable amount of W. TEM analysis of the spent samples (Figure S3) revealed plate-like shapes with particles spread across the support with sizes of tens of nanometers. In addition, both TEM and SEM images confirm the lack of porosity in the calcined catalysts, in agreement with the BET measurements.

The catalysts were further studied with EDS mapping technique to gain information on the elemental dispersions. In general, the utilization of MCF-17 achieved good overall elemental dispersion, owing to its high surface area and pore volume as well as the ordered pore structure, which could provide significantly more sites than the regular silica-gel to homogeneously distribute the supported metals and inhibit their aggregation to achieve better fixation. More specifically, elemental mapping results (Figure 1, third to sixth columns) indicate a near-homogeneous distribution of W and Na with minor formation of W-rich or Na-rich areas. On the other hand, Mn shows poorer dispersion and has a higher tendency to form small aggregates, particularly for the original and Pt-doped samples. Since the loadings of the noble metals are lower than Mn and W, the signal level is weaker. Nevertheless, results indicate homogeneous distributions of the noble metals, with no obvious aggregation or particle formation of significant sizes observed. This is also in accordance with the fact that no noble metal containing species were observed in the XRD spectra of the doped catalysts. Among the four catalysts, the Rh-doped sample shows the best overall elemental dispersion, especially for Mn.

3.1.4. XRD measurements

In order to study the phase composition, XRD measurements were conducted on both the fresh and spent catalysts. The diffraction patterns of the fresh samples are shown in Figure 2a. Na₂WO₄ and Mn₂O₃ phases were clearly identified and are the main form of tungsten and manganese oxide, respectively. While most of the tungsten species exist as Na₂WO₄, features due to Na₄WO₅ were also detected. Unlike

the amorphous nature of the silica support MCF-17, strong diffraction peaks associated with α -cristobalite were observed in the calcined catalysts. In addition, a small amount of tridymite was also detected, as indicated by the diffraction peak at 20.6 \circ . The transformation of amorphous silica to α -cristobalite during the high temperature calcination process is facile with Na present, especially aided with W, and is well known for the Mn_xO_y-Na₂WO₄/SiO₂ system. [23] The phase transformation is also accompanied by a significant loss of pore volume and surface area, as shown in Table 1. It is also noted that no noble metalcontaining crystal phases were observed for the doped catalysts, which could be explained by the low degree of metal loading and the insensitivity of X-ray diffraction to small clusters. Despite the slight variation in the intensity of the diffraction peaks, no significant difference in the phase composition was observed among the four catalysts.

In the spent samples (Figure 2b), MnWO₄ was identified in addition to Mn₂O₃, while peaks due to Na₄WO₅ disappeared after the reaction. The transformation of Mn₂O₃ to MnWO₄ indicates a partial reduction of Mn³⁺ to the more stable Mn²⁺, which could be involved in the total catalytic cycle. However, its exact contribution to the catalytic performance is still unclear. One plausible mechanism involves the activation of oxygen and methane on Mn²⁺ and WO₄²⁻ sites, respectively. The spillover of the activated surface oxygens from Mn sites to W sites replenishes the active centers for methane activation and keeps the catalyst active. [7] [24] In addition, α -cristobalite remains as the primary silica phase. It should be noted that the appearance of the quartz phase in the spent samples could have mainly originated from the quartz sand residue, which was used to dilute the catalyst in the catalytic bed, and is therefore not the result of the transformation from other forms of silica during the reaction. Nonetheless, its formation could not be completely ruled out.

Using the Scherrer equation, the average sizes of the catalyst particles could be estimated (Table S1). The results indicate the growth of both Mn_2O_3 and Na_2WO_4 particles after the catalytic measurements. Among the four catalysts tested, the Rh-doped catalyst exhibited the biggest change in the Mn_2O_3 particle sizes before and after the reaction, with about 12 nm growth being observed.

3.1.5. XPS analysis

Surface analysis of the prepared catalysts is carried out using XPS. Figure 3 shows the XPS spectra of W 4f and Mn 2p level of the fresh catalysts. Binding energies of W $4f_{7/2}$ and Mn $2p_{3/2}$ peaks are in the range of 35.0-35.2 eV and 641.7-642.1 eV, which are assigned to the corresponding species in Na₂WO₄ and Mn₂O₃, respectively. [22,25] It is noted that the W 4f and Mn 2p spectra of the doped catalysts (35.0 eV for W $4f_{7/2}$ and 641.7 eV for Mn $2p_{3/2}$ peaks) shifted ~0.2 eV and ~0.4 eV, respectively, towards lower binding energy as compared to those of the original sample (35.2 eV for W $4f_{7/2}$ and 642.1 eV for Mn

 $2p_{3/2}$ peaks), which indicates a more reduced nature of the W and Mn species on the surface of the doped catalysts.

Information on the surface compositions are shown in Table 3. For the fresh catalysts, comparable amounts of Na were found on the surface of both the doped and undoped samples. As for the Mn concentration, the Rh-doped catalyst showed the highest value, while similar loadings were observed for the others. The Rh-doped catalyst also displayed the highest W concentration among the four catalysts, followed by the Pt-doped and undoped samples, with the Ir-doped one exhibited the lowest surface W content. This is in accordance with the finding from other researchers that the Mn surface concentration increases with the W concentration. [9][26] The most noticeable difference in the surface concentration is observed for Mn, while the variation in the surface W content is less than 10% among the four catalysts. S.-f. Ji et al. reported an optimum surface Mn content of 1.1% for C₂ production on Mn_xO_y-Na₂WO₄/SiO₂ catalysts with similar bulk composition, below which a higher Mn surface concentration would be beneficial. [9] This agrees with the high C₂ selectivity (Figure 5b) for the Rh-doped catalyst, which has the highest surface Rh concentration of 0.84%. Again, due to the quartz sand residue, the surface concentrations reported for the spent catalysts should be taken as their lower limit, and therefore only the change in the surface C concentration could be discussed without ambiguity. The spent catalysts showed significantly more amount of carbon on their surfaces after the reaction, with the increase in the order of Original \approx Ptdoped > Ir-doped > Rh-doped samples. This is also in agreement with the degree of carbon balance during the reaction. The Rh-doped catalyst showed the best carbon balance of ~98%, followed by the Ir-doped catalyst at \sim 94%, while the original and Pt-doped catalysts have the lowest value of \sim 91%.

3.1.6. H₂-TPR analysis

Figure 4 shows the H₂-TPR results for the fresh catalysts. The reduction peaks in the range of 300 °C to 650 °C are associated with the reduction of Mn. The broadness of the peak and the shoulder feature indicate the coexistence of different Mn species. The broad feature starting from 700 °C represents the reduction of the W species in the catalysts. [23,27] As compared to the undoped Mn_xO_y -Na₂WO₄/SiO₂ sample, the incorporation of noble metals facilitates the reduction of Mn, as indicated by the higher intensity of the Mn reduction features between 300 °C to 650 °C and their shift to lower temperatures, especially for the Rh-doped catalyst. The change in the reducibility could also be due to a better dispersion of the MnO_x species, [28] as is in accordance with the EDS mapping results. On the other hand, the Pt-doped and Ir-doped catalysts showed the W reduction feature at more than 20 °C lower in temperature than the Rh-doped sample.

3.2. Catalytic measurements

The catalysts, after being pelletized and sieved, were utilized in the OCM reaction. Figure 5a shows the reaction conversion as a function of time on stream. Among the four catalysts tested, the undoped Mn_xO_y -Na₂WO₄/MCF-17 catalyst showed the highest conversion at 15.6%. The introduction of noble metal dopants led to a slight decrease in the CH₄ conversion, with that of the Pt-doped, Ir-doped, and Rh-doped catalysts being at 14.1%, 14.4%, and 9.3% (Table 4). No significant deactivation was observed for the catalysts during the time period (~12 h) tested.

The product distribution for all the catalysts are shown Figure 5b. C₂ hydrocarbons (C₂H₄ and C₂H₆) and CO_x (CO and CO₂) make up the majority of the reaction products (>90%). A small amount (~4-6% in selectivity) of C₃s (C₃H₆ and C₃H₈), which are due to the further chain growth of C₂ hydrocarbons, are also observed. The incorporation of noble metals improved the selectivity towards both C₂ and C₃ hydrocarbons in the order of Rh-doped > Ir-doped > Pt-doped catalyst. The doped catalysts also showed lower C₂H₄/C₂H₆ and C₃H₆/C₃H₈ ratios as compared to their undoped counterpart. The olefin to paraffin ratio for both C₂s and C₃ follows the same trend, in which the Rh-doped catalyst offers the lowest value, followed by the Ir-doped and Pt-doped catalysts, while the original sample shows the highest percentage of unsaturated products. The decrease in the olefin to paraffin ratio for the noble metal doped catalysts indicates a less favorable ethane dehydrogenation process.

The yield of different products are shown in Figure 6b. It can be seen from Figure 6b that the Ir-doped catalyst showed the highest overall yield for C_2 and C_3 hydrocarbons. The Rh-doped sample, having the highest selectivity, exhibited a smaller degree of improvement on the C_2 yield due to a slightly lower conversion. The Pt-doped and the undoped samples displayed similar activity towards overall C_2 production. Since the catalysts were tested under the same conditions, non-catalytic gas phase reactions should contribute in a similar way. Therefore the difference in the dehydrogenation ability is more likely due to the variation in the surface properties of the catalysts. All the catalytic results are also summarized in Table 4.

Since the ICP-AES (Table 2), BET (Table 1), and XRD (Figure 2) measurements all showed similar results, the difference in the catalytic behavior, especially the enhancement of C_2 selectivity for the doped catalysts could hardly be explained by the difference in their structural and compositional characteristics. It is commonly agreed that the OCM reaction proceeds via a heterogeneous-homogeneous mechanism, where ethane is primarily formed through the gas-phase recombination of methyl radicals that are generated through surface reactions. Ethylene is then formed via the dehydrogenation of ethane either homogeneously or heterogeneously. CO_x , on the other hand, is produced from the consecutive oxidation of either the methyl radicals or the C_2 products. [29] The enhancement of C_2 selectivity implies a restraint

on these deep oxidation reactions, which could result from a more optimized strength of interaction between the carbon intermediate species and the surface of the catalyst, which allows them to desorb readily into the gas phase without being further consumed by the surface oxygen. [30] This is evidenced by the fact that there is significantly less amount of carbon left on the surface of the noble metal doped catalysts after the reaction (Table 3) and also lower olefin to paraffin ratios obtained on these catalysts (Table 4).

In addition, the change in the redox property of the oxide species (Figure 4) would alter the electronic structure at the surface of the catalysts, thus affecting the strength of their interaction with the reaction intermediates, which could also be part of the reason for the enhanced performance. As has been mentioned in section 3.1.4, the reaction involves the activation of oxygen on the Mn^{2+} sites. The improvement of the reducibility of Mn species would imply an increased ability to activate oxygen. On the other hand, the activation of methane occurs mainly on the $WO4^{2-}$ sites, to which a facile reduction of the W species would be beneficial. The Rh-doped catalyst showed the Mn reduction feature at the lowest temperature, followed by the Ir-doped sample. On the other hand, the Ir-doped and Pt-doped catalysts showed higher degree of reduction of W than the Rh-doped sample at the temperature (750 °C) where the catalytic measurements were carried out. These two factors together result in a higher overall C₂ yield for the Ir-doped catalyst. The Rh-doped sample, although having Mn reduction peak at the lowest temperature, showed smaller amount of enhancement in the overall C₂ yield due to a more difficult reduction of WO4²⁻ species, which would lead to a weaker methane activation process.

4. Conclusions

To summarize, noble metal doped M-Mn_xO_y-Na₂WO₄/MCF-17 (M = Pt, Ir, Rh) catalysts with similar elemental compositions were prepared via a wet impregnation method, and their performance in the OCM reaction was tested. When compared to the undoped Mn_xO_y -Na₂WO₄/MCF-17 catalyst, the incorporation of the noble metals enhanced the selectivity towards both C₂ and C₃ hydrocarbons in the order of Rh-doped > Ir-doped > Pt-doped catalyst and offered lower olefin to paraffin ratios. On the other hand, the Ir-doped catalyst showed the highest C₂ yield, followed by the Rh-doped sample. Since no significant difference between the original and the doped catalysts was observed in terms of elemental loading, surface area, and phase composition, the enhanced OCM performance was attributed to a more optimized strength of interaction between the carbon intermediate species and the surface of the noble metal doped catalysts in combination with an improved reducibility of W and Mn species and metal dispersion.

Acknowledgment

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, U.S. Department of Energy, under Contract DE-AC02-05CH11231, through the Chemical and Mechanical Properties of Surfaces, Interfaces and Nanostructures program (FWP KC3101). The XPS and TEM/EDS measurements were conducted in Molecular Foundry at Lawrence Berkeley National Laboratory under user proposal #4435, which is supported, by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Authors also acknowledge Zeqiong Zhao for her generous help with the SEM measurements.

Reference

- M.C. Alvarez-Galvan, N. Mota, M. Ojeda, S. Rojas, R.M. Navarro, J.L.G. Fierro, Catal. Today 171 (2011) 15–23.
- [2] A. Galadima, O. Muraza, J. Ind. Eng. Chem. 37 (2016) 1–13.
- [3] C. Hammond, S. Conrad, I. Hermans, ChemSusChem 5 (2012) 1668–1686.
- [4] J.H. Lunsford, Angew. Chemie Int. Ed. English 34 (1995) 970–980.
- [5] V.I. Alexiadis, M. Chaar, A. van Veen, M. Muhler, J.W. Thybaut, G.B. Marin, Appl. Catal. B Environ. 199 (2016) 252–259.
- [6] U. Zavyalova, M. Holena, R. Schlögl, M. Baerns, ChemCatChem 3 (2011) 1935–1947.
- S. Arndt, T. Otremba, U. Simon, M. Yildiz, H. Schubert, R. Schomäcker, Appl. Catal. A Gen. 425–426 (2012) 53–61.
- [8] J. Wang, L. Chou, B. Zhang, H. Song, J. Zhao, J. Yang, S. Li, J. Mol. Catal. A Chem. 245 (2006) 272–277.
- [9] S. Ji, T. Xiao, S. Li, C. Xu, R. Hou, K.S. Coleman, M.L. Green, Appl. Catal. A Gen. 225 (2002) 271–284.
- [10] M. Yildiz, Y. Aksu, U. Simon, K. Kailasam, O. Goerke, F. Rosowski, R. Schomäcker, A. Thomas,
 S. Arndt, Chem. Commun. 50 (2014) 14440–14442.
- M. Yildiz, Y. Aksu, U. Simon, T. Otremba, K. Kailasam, C. Göbel, F. Girgsdies, O. Görke, F. Rosowski, A. Thomas, R. Schomäcker, S. Arndt, Appl. Catal. A Gen. 525 (2016) 168–179.
- [12] J.A. Labinger, J.E. Bercaw, Nature 417 (2002) 507–14.
- [13] J. Wencel-Delord, T. Dröge, F. Liu, F. Glorius, Chem. Soc. Rev. 40 (2011) 4740–4761.
- [14] A.A. Latimer, A.R. Kulkarni, H. Aljama, J.H. Montoya, J.S. Yoo, C. Tsai, F. Abild-Pedersen, F. Studt, J.K. Nørskov, Nat. Mater. 1 (2016) 1–6.
- [15] C.-C. Wang, S.S. Siao, J. Jiang, J. Phys. Chem. C 116 (2012) 6367–6370.
- [16] T.L.M. Pham, E.G. Leggesse, J.C. Jiang, Catal. Sci. Technol. 5 (2015) 15–18.

- [17] Y. Han, S.S. Lee, J.Y. Ying, Chem. Mater. 19 (2007) 2292–2298.
- [18] N. Musselwhite, K. Na, K. Sabyrov, S. Alayoglu, G.A. Somorjai, J. Am. Chem. Soc. 137 (2015) 10231–10237.
- [19] W.-C. Liu, G. Melaet, W.T. Ralston, S. Alayoglu, Y. Horowitz, R. Ye, T. Hurlburt, B. Mao, E. Crumlin, M. Salmeron, G.A. Somorjai, Catal. Letters 146 (2016) 1574–1580.
- [20] G. Melaet, W.T. Ralston, C.-S. Li, S. Alayoglu, K. An, N. Musselwhite, B. Kalkan, G.A. Somorjai, J. Am. Chem. Soc. 136 (2014) 2260–2263.
- [21] S.-F. Ji, T.-C. Xiao, S.-B. Li, C.-Z. Xu, R.-L. Hou, K.S. Coleman, M.L.H. Green, Appl. Catal. A Gen. 225 (2002) 271–284.
- [22] Y. Kou, B. Zhang, J. Niu, S. Li, H. Wang, T. Tanaka, S. Yoshida, J. Catal. 173 (1998) 399–408.
- [23] A. Palermo, J.P. Holgado Vazquez, A.F. Lee, M.S. Tikhov, R.M. Lambert, J. Catal. 177 (1998) 259–266.
- [24] P. Wang, G. Zhao, Y. Wang, Y. Lu, Sci. Adv. 3 (2017) e1603180.
- [25] H.W. Nesbitt, D. Banerjee, Am. Mineral. 83 (1998) 305–315.
- [26] T.W. Elkins, H.E. Hagelin-Weaver, Appl. Catal. A Gen. 497 (2015) 96–106.
- [27] R. Koirala, R. Büchel, S.E. Pratsinis, A. Baiker, Appl. Catal. A Gen. 484 (2014) 97–107.
- [28] Y. Liu, M. Luo, Z. Wei, Q. Xin, P. Ying, C. Li, Appl. Catal. B Environ. 29 (2001) 61-67.
- [29] E. V. Kondratenko, M. Baerns, in:, E. Ertl, G., Knozinger, H., Schuth, F., Weitkamp, J (Ed.), Handb. Heterog. Catal., 2nd ed., Wiley-VCH, Weinheim, 2008, pp. 3010–3023.
- [30] G. Kumar, S.L.J. Lau, M.D. Krcha, M.J. Janik, ACS Catal. 6 (2016) 1812–1821.



Figure 1. Column 1: TEM images; Column 2: high-angle annular dark-field (HAADF) images; Columns 3-6: EDS elemental mapping results (Na: green, Mn: red, W: blue, and noble metals: yellow) of the fresh M-Mn_xO_y-Na₂WO₄/MCF-17 catalysts: a) Original; b) M = Rh; c) M = Ir; d) M = Pt.



Figure 2. XRD patterns of the a) fresh and b) spent catalysts. Sample names are listed under their corresponding spectra. The file numbers in the PDF database used for phase identification are listed after the name of the compound.



Figure 3. XPS spectra of a) W 4f and b) Mn 2p level for the fresh $M-Mn_xO_y-Na_2WO_4/MCF-17$ catalysts: i) Original; ii) M = Rh; iii) M = Ir; iv) M = Pt. A spin-orbital splitting of 2.17 eV and an area ratio for W $4f_{7/2}$ (red) and W $4f_{5/2}$ (blue) peaks of 4:3 were used when fitting the W 4f spectra. Due to the low signal-to-noise ratio, fitting was not performed on the Mn 2p spectra.



Figure 4. H₂-TPR profiles of the fresh catalysts. Sample names are listed under their corresponding scans. A high purity mixture of 5% H₂/Ar was used as the reducing gas with a flow rate of 30 sccm. The reactor was heated to 850 °C with a heating rate of ~6°C/min.



Figure 5. a) Reaction conversion as a function of time on stream and b) reaction selectivity of C_2 , C_3 , and CO_x for all the catalysts in the OCM reaction. Reaction conditions: feed composition of $CH_4:O_2:N_2 = 4:1:4$, total flow rate of 60 sccm, and reaction temperature of 750 °C. Selectivity is in terms of carbon.



Figure 6. a) Conversion-Selectivity plot and b) Reaction yield for all the catalysts in the OCM reaction. Reaction conditions: feed composition of $CH_4:O_2:N_2 = 4:1:4$, total flow rate of 60 sccm, and reaction temperature of 750 °C.

Table 1. BET surface area and tot	al pore volume of MC	F-17 and the prepa	red catalysts
-----------------------------------	----------------------	--------------------	---------------

	MCF-17	Original	Rh-doped	Ir-doped	Pt-doped
BET surface area/m ² ·g ⁻¹	566.3 ± 4.9	9.18 ± 0.04	8.91 ± 0.02	8.19 ± 0.03	7.59 ± 0.02
Total pore volume ^a /cm ³ ·g ⁻¹	1.598	0.024	0.024	0.021	0.017
Average pore size ^b /nm	16.6	-	-	-	-

^aBJH adsorption cumulative volume of pores; ^bBJH adsorption pore size

		5					
Elemental Composition	Theoretical Loading/wt %	Determined Loading ^a /wt.%					
		Original	Rh-doped	Ir-doped	Pt-doped		
Na	0.78 ^b	0.73	0.78	0.72	0.79		
W	3.13 ^b	2.51	2.23	2.29	2.48		
Mn	2.00 ^c	2.04	2.04	2.23	2.37		
Rh	0.10	-	0.13	-	-		
Ir	0.10	-	-	0.12	-		
Pt	0.10	-	-	-	0.12		

Table 2. Theoretical and determined loadings of the prepared catalysts

^aAs determined from ICP-AES; ^bCorresponds to 5 wt.% of Na₂WO₄; ^cCalculated in terms of elemental Mn

	C 1s/%		Na 1s/%		Mn 2p/%		W 4f/%	
-	Fresh	Spent ^b	Fresh	Spent ^b	Fresh	Spent ^b	Fresh	Spent ^b
Original	9.6	52.3	0.27	0.14	0.53	0.13	0.89	0.65
Rh-doped	9.3	37.8	0.28	0.20	0.84	0.27	1.03	0.71
Pt-doped	8.3	50.1	0.26	0.13	0.56	0.16	0.91	0.50
Ir-doped	12.4	42.7	0.32	0.21	0.56	0.13	0.83	0.68

Table 3. Surface compositions^a of the fresh and spent catalysts.

^aAs obtained from XPS; ^bDue to the quartz sand residue, the surface concentrations reported for the spent catalysts should be taken as their lower limits

Table 4. OCM activity and selectivity after ~12h of time on stream^a.

Catalysts	CH ₄ Conversion/%	Selectivity ^b /%					
		C ₂	C ₃	CO _x	C2H4/C2H6	C3H6/C3H8	
Original	15.6	33.0	4.0	57.3	3.6	4.4	0.11
Rh-doped	9.3	55.6	5.6	36.7	0.93	1.4	1.1
Ir-doped	14.4	46.7	4.8	46.0	1.5	3.0	0.30
Pt-doped	14.1	36.1	4.0	57.1	2.8	4.7	0.12

^aReaction conditions: feed composition of CH₄:O₂:N₂ = 4:1:4, total flow rate of 60 sccm, and reaction temperature of 750 °C; ^bSelectivity is in terms of carbon.