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Metal-Doped Mesoporous MnO₂-CeO₂ Catalysts for Low-Temperature Pre-Oxidation of NO to NO₂ in Fast SCR Process

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Abstract: Selective catalytic reduction (SCR) is an effective system for treating nitrogen oxides (NO_x; mainly NO), and fast SCR requires the equimolar reactants of NO and NO₂. This study focused on catalysts for oxidizing 50% of NO to NO₂. A series of catalysts composed of a variety of components, such as mesoporous mMnO₂-nCeO₂ as carrier catalysts (m:n = 9:1 and 7:3) and transition metals (e.g., Fe, Co, Ni, Cu, and Cr), were synthesized and characterized using N₂ adsorption, in situ XRD, TEM, and XPS. All samples had a mesoporous structure with pore size around 8 nm. XPS results demonstrated that addition of cerium ion increased the surface area and provided oxygen vacancy due to the formation of Ce³⁺ within the structure. NO oxidation activity was tested using a feed (205~300 ppm NO and 6% O₂) that simulated typical flue gas conditions. Doped mesoporous mMnO₂-nCeO₂ has higher NO oxidation activity than pristine mMnO₂-nCeO₂. The doped mMnO₂-nCeO₂ catalyzed 50% of NO to NO₂ at between 140 and 200 °C resulting in an equivalent amount of NO and NO₂. Among the transition metals, Cu, Ni, Co, Fe, and Cr have the highest to lowest oxidation activity, respectively. The precatalytic oxidation of NO can potentially be combined with the current SCR system without changes to existing equipment and can be applied to the exhaust gas treatment for de-NO_x.



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Keywords: mesoporous MnO₂-CeO₂; NO oxidation; doped catalysts

1. Introduction

Atmosphere nitric acid or particulate nitrate formed from the oxidation of nitrogen oxides (NO_x; mainly NO) constitute precursors of fine suspended particles (PM_{2.5}). PM_{2.5} contributes to cancer, cardiovascular disease, and other critical health problems. Therefore, countries worldwide have enacted regulations to address PM_{2.5} pollution, which include the strict control of PM_{2.5} precursor emissions. Within the European Union, the National Emission Ceilings Directive agreed that emissions of the four major pollutant species must comply with the upper limit [1] stipulated by the Gothenburg Protocol. These four species are NO_x, sulfur dioxide (SO₂), non-methane volatile organic compounds, and ammonia (NH₃).

Much research and investment has focused on the reduction of NO_x content in industrial waste gas. Bosch and Janssen [2] proposed a variety of methods for removing nitrogen oxides in 1988. Two types of NO_x removal methods are currently employed, selective catalytic reduction (SCR) [3] and selective noncatalytic reduction (SNCR), both of which are relatively mature technologies and require NH₃ as a reduction agent. SNCR requires no catalysis, and its reaction temperature ranges from 850–1100 °C, consuming a relatively high amount of energy; SCR uses V₂O₃/WO₃ catalysts and has a reaction temperature between 300–400 °C. Researchers have dedicated decades of work to the development of these two technologies. SCR technology has been adopted in the treatment of diesel engine exhaust emissions.

SCR is one of the most effectively adopted treatment techniques for NO_x (NO, NO₂, and N₂O; NO accounts for >95% in most emission sources) abatement with an efficiency of up to 90% in the power generation, steel, cement, and paper and pulp industries. Currently, metal oxide catalysts such as V₂O₅-WO₃/TiO₂ are the most widely used; however, commercial metal oxide catalysts must operate at high temperatures (300–400 °C) and require the oxidation of SO₂ to SO₃, which results in the formation of black viscous liquid ammonia bisulfide (NH₄HSO₄) with NH₃, rendering further catalysis ineffective. Conversely, the development of low-temperature SCR (LT-SCR) solves the aforementioned problems because it can be located downstream of the electrostatic precipitator. However, the drawbacks of LT-SCR include potential poisoning by H₂O or SO₂ and the formation of the undesired byproduct N₂O [4,5]. Thus, achieving a balance between traditional SCR and LT-SCR remains challenging.

The main SCR chemical reaction converts NO_x into N₂ and H₂O (reaction 1). The temperature must be controlled between 300–400 °C to effectively remove >90% NO_x. Studies on NO catalysis [6,7] have indicated that if 50% of the NO of pollutants can be converted into NO₂, the reaction rate of fast SCR (reaction 2) is 10 times faster with equimolar amounts of NO and NO₂ [8] compared with the main SCR reaction and it operates effectively at 200 °C. Therefore, when the equimolar oxidation of NO can be achieved below 200 °C, the SCR [9], the reaction route can be changed from main SCR to fast SCR; the lower reaction temperature of approximately 200 °C results in energy savings and commercial applicability without changes to the currently used process.



Three types of SCR systems are used to treat flue gas [10] according to its relative position in the treatment system. They include high-dust SCR, low-dust SCR, and tail-end SCR (Figure 1). High-dust SCR has a market share of 88% because the inlet flow temperature easily reaches the required reaction temperature of traditional SCR (350–400 °C). However, the flue gas comprises particles, NO_x, and SO_x; blockage of the pores on the catalyst surface by the particles and its subsequent deactivation necessitates the regular use of soot blowers and sonic horns to clean the catalyst bed. Furthermore, a continually high reaction temperature causes catalyst agglomeration and a higher fuel consumption cost [11,12]. Second, low-dust SCR, which is located behind the EP (electrostatic precipitator), accounts for approximately 6% of all instances of SCR in use. Low-dust SCR has intake air containing NO_x and SO_x without particles and does not require a hopper to collect particles; although this allows for reduced SCR system volume, the inlet airflow must be reheated with an economizer to maintain de-NO_x efficiency. Furthermore, the inlet flue gas still contains SO_x; after increasing NH₃ to improve NO_x removal efficiency, the formation of ammonia bisulfide occurs, blocking the catalyst, as is the case in high-dust SCR. Finally, tail-end SCR, which also accounts for only 6% of the SCR types, has only NO_x at the inlet air flow, and the air flow temperature generally drops to 150–290 °C depending on the efficiency at which process heat is recovered; the temperature can sometimes drop to approximately 80 °C, requiring only 50% of the catalyst [13] in high-dust SCR, resulting in a doubled catalyst lifetime. However, tail-end SCR requires the installation of heat recovery and heating equipment to reach the reaction temperature. Therefore, if the de-NO_x process can be completed at approximately 200 °C without changes to the current SCR catalyst and the installation of new equipment (i.e., only with modified pipelines), it constitutes a feasible improvement to flue gas treatment systems from high-dust SCR to tail-end SCR in terms of energy savings, catalyst cost [14], and catalyst lifetime.

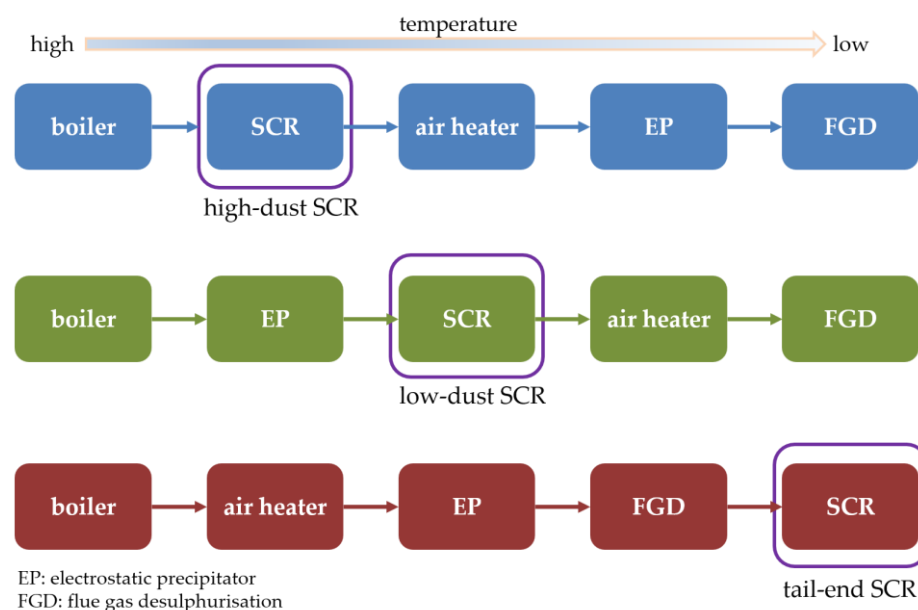


Figure 1. Types of SCR in the flue gas treatment system.

Various catalysts for NO oxidation to NO₂ have been developed mostly in supported catalysts doped with a noble metal such as Pt [15], Pd [16], and Ru [17], or in perovskite type [18,19]. These two categories were restricted from field application due to their high price and costly synthesis procedure, respectively. MnO₂ has been widely studied as well due to its low cost, environmental benefits, and relatively high activity for catalytic oxidation [20,21]. Mesoporous materials have also been widely used as catalyst carriers because of their large specific surface area, interconnected channels, and well-defined pore diameters [22,23]. These three-dimensional (3D) structural catalysts using KIT-6 as a template have been found to generate abundant active sites and mass transfer, thus enabling effective oxidation. Besides, with high redox properties and the lability of lattice oxygen, ceria (CeO₂) shows high catalytic activity. Ceria also possesses high oxygen storage capacity, which allows for using the oxide not only as a support but also as a catalyst for oxidation. The present study developed a selective NO oxidation catalyst comprising mainly mesoporous MnO₂ and CeO₂ doped with economic transition metal as a pre-oxidation catalyst for SCR to partially convert 50% NO to NO₂ and to lower the SCR reaction temperature to 200 °C with promising NO removal efficiency (Figure 2).

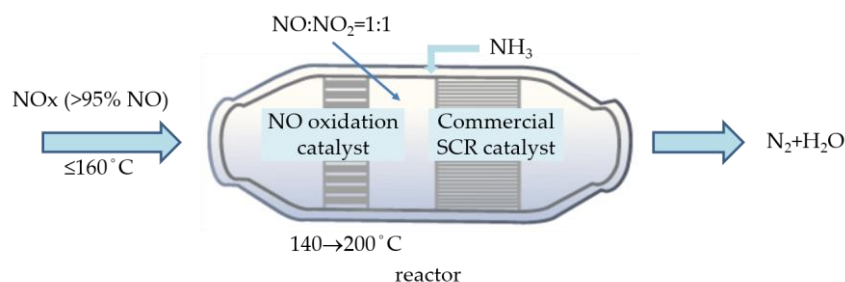


Figure 2. Reaction configuration of SCR with NO oxidation and commercial catalyst.

2. Results and Discussion

This study used a mesoporous metal oxide coated with trace amounts of transition metals as dopants as a carrier catalyst to synthesize a selected low-temperature NO catalyst; its composition was DP/mMnO₂-nCeO₂ (m:n = 9:1 and 7:3, wherein the coated metal (DP) could be Fe, Co, Ni, Cu, and Cr). The KIT-6-template was adopted to obtain 3D ordered mesoporous metal oxide (mMnO₂-nCeO₂). All mMnO₂-nCeO₂ catalysts were doped with DP at 1 atomic%. The catalysts in this study primarily served to catalyze 50%

NO to NO₂ at a temperature between 140 and 200 °C and to reduce the traditional SCR reaction temperature to 200 °C, resulting in energy savings, catalyst lifetime extension, and application flexibility. Several additional mesoporous metal oxides were concurrently synthesized to compare their NO oxidation capability with the doped mMnO₂-nCeO₂.

2.1. Characterization of NO_x Oxidation Catalysts

Two major mesoporous metal oxides were synthesized as catalyst carriers for NO oxidation to NO₂, namely, mMnO₂-nCeO₂ (m:n = 9:1 and 7:3 as mole ratio in synthesis). Ce was employed as a component carrier due to its high oxygen storage capacity, excellent tolerance to H₂O and SO₂, environmental benefits, and low cost [24].

2.1.1. Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD) Analysis

XRD analysis was used to verify the crystallographic structure of mMnO₂-nCeO₂ (m:n = 9:1 and 7:3) catalysts. XRD patterns revealed broad peaks indicating a low crystallinity of both catalysts. As illustrated in the left image of Figure 3, the 2θ peaks (varying from 20° to 100°) of 7MnO₂-3CeO₂ at 28.8°, 33.4°, 37.3°, 42.8°, 47.9°, 56.9°, 59.6°, and 72.5° corresponded to the combination from (110) of MnO₂ (PDF-ICDD-04-005-4881, β-MnO₂) and (111) of CeO₂ (PDF-ICDD-01-083-4917), (200) of CeO₂, (101) of MnO₂, (111) of MnO₂, (220) of CeO₂, the combination from (211) of MnO₂ and (311) of CeO₂, and (301) and (112) of MnO₂. The diffraction peaks of 9MnO₂-1CeO₂ illustrated in the right image of Figure 3 are in accordance with those of MnO₂; they display no traces of the CeO₂ pattern, which indicates an amount of Ce ions so small that their diffraction patterns are covered by those of MnO₂. Moreover, crystallites exhibit wide diffraction peaks; in Figure 3, the SEM images of synthesized crystals reveal irregular shapes with various grain sizes indicative of lower crystallinity.

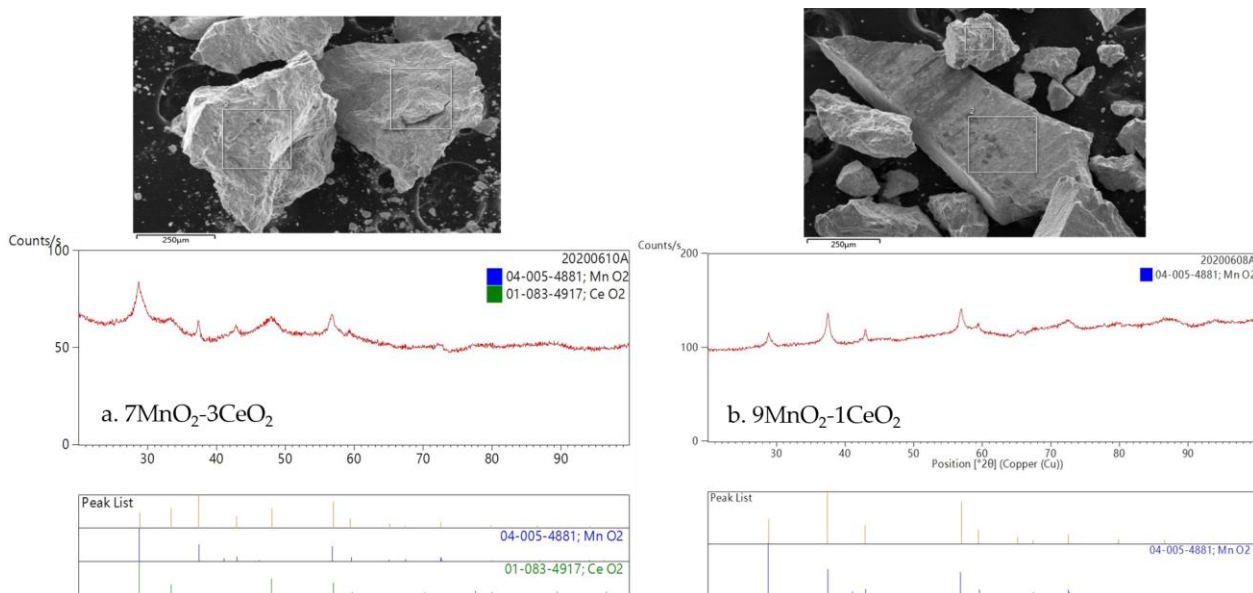


Figure 3. SEM images and XRD patterns of (a) 7MnO₂-3CeO₂ and (b) 9MnO₂-1CeO₂ catalysts.

2.1.2. Physical Characteristics Analysis

The BET surface areas, pore volumes, and pore sizes of 7MnO₂-3CeO₂ and 9MnO₂-1CeO₂ catalysts are summarized in Table 1; two other porous pristine MnO₂ and CeO₂ synthesized with KIT-template in previous work [25] are included as well for comparison. It can be seen that the surface area of pure CeO₂ was two times larger than pure MnO₂. The addition of cerium ions to MnO₂ helped increase its surface area. As the added ceric molar ratio increased from 10% to 30%, the surface area of catalyst rose from 87.3 to 124.2 m²/g. Both 9MnO₂-1CeO₂ and 7MnO₂-3CeO₂ showed a similar average pore size

with that of pure MnO_2 , while their pore volumes were significantly increased with the increasing proportion of cerium oxide. It is noteworthy that the pores of all the samples were meso-pores (between 2 and 50 nm).

Table 1. BET surface areas, pore volumes, and pore sizes of catalysts synthesized from KIT-6.

Catalyst	S_{BET} (m^2/g)	D_{pore} (nm)	V_{pore} (cm^3/g)	Refs.
MnO_2	61.5	8.7	0.13	[25]
$9\text{MnO}_2\text{-}1\text{CeO}_2$	87.3	8.2	0.18	this work
$7\text{MnO}_2\text{-}3\text{CeO}_2$	124.2	7.3	0.23	this work
CeO_2	135.0	12.8	0.43	[25]

The Mn, Ce, and doped transition metal (Co, Ni, Fe, Cu, Cr) contents of as-synthesized catalysts were investigated by ICP-OES, as shown in Table 2. The ICP results demonstrated that the Mn/Ce atom ratio was 8.77 for $9\text{MnO}_2\text{-}1\text{CeO}_2$ and that all the doped $9\text{MnO}_2\text{-}1\text{CeO}_2$ catalysts possessed similar Mn/Ce atom ratios between 9.01 and 9.14, which indicates their consistency with theoretical values. Although the (Mn + Ce)/corresponding dopant atom ratios varied from roughly 65 to 99, considered as experimental deviation due to the large gap between the dopant and Mn–Ce supporter, elemental mappings (Section 2.1.3) of Co, Ni, Fe, Cu, and Cr revealed that all DPs were full-dispersedly doped into their corresponding Mn–Ce catalysts.

Table 2. Catalyst component content analysis from ICP-OES.

Catalyst	Mn/Ce Atom Ratio	(Mn + Ce)/DP Atom Ratio DP = Doped Metal
$9\text{MnO}_2\text{-}1\text{CeO}_2$	8.77	-
Co/ $9\text{MnO}_2\text{-}1\text{CeO}_2$	9.14	71.9
Ni/ $9\text{MnO}_2\text{-}1\text{CeO}_2$	9.21	66.8
Fe/ $9\text{MnO}_2\text{-}1\text{CeO}_2$	9.11	71.4
Cu/ $9\text{MnO}_2\text{-}1\text{CeO}_2$	9.19	64.6
Cr/ $9\text{MnO}_2\text{-}1\text{CeO}_2$	9.01	99.6

2.1.3. Transmission Electron Microscopy (TEM) and Energy-Dispersive X-ray Spectroscopy (EDS) Results

To investigate the synthesized catalysts' structural and chemical uniformity, high-resolution TEM (HRTEM) and EDS were performed. As shown in Figure 4a–c, typical TEM images were taken at different magnifications. Figure 4a illustrates that $9\text{MnO}_2\text{-}1\text{CeO}_2$ had the same structural properties as porous MnO_2 , indicating that the addition of Ce did not affect catalyst synthesis by using KIT-6 as a hard template [26]. The average pore diameter of $9\text{MnO}_2\text{-}1\text{CeO}_2$ measured 8.7 nm, which complied with the BET results of $9\text{MnO}_2\text{-}1\text{CeO}_2$ listed in Table 1 and was consistent with that of mesoporous MnO_2 synthesized from the KIT-6 template. Moreover, after magnifying the framed spectrum image in 4c, EDS elemental mapping of Mn (Figure 4d) and Ce (Figure 4e) also verified highly-dispersed CeO_2 in MnO_2 .

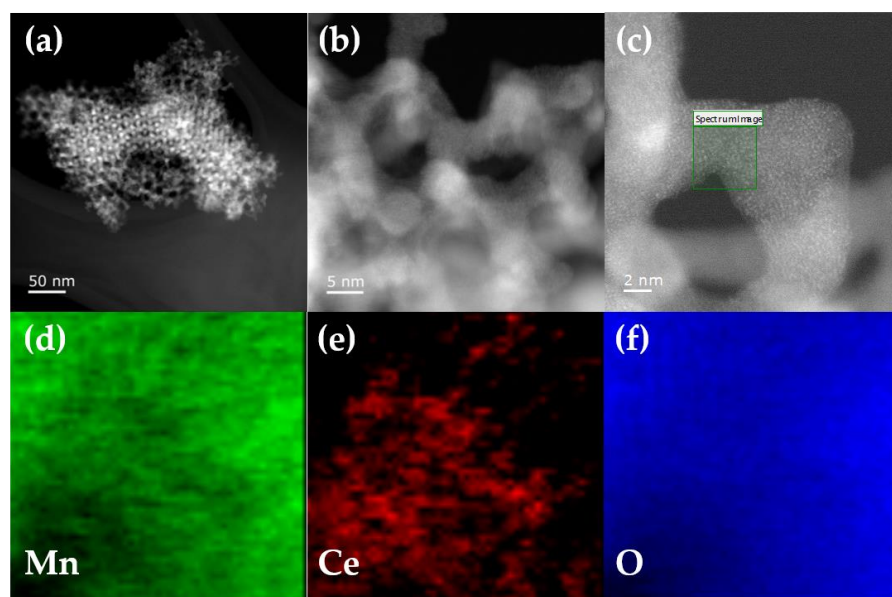


Figure 4. (a,b) TEM image of 9MnO₂–1CeO₂. (c) EDS elemental mapping of (d) Mn, (e) Ce, and (f) O for 9MnO₂–1CeO₂ catalyst.

EDS elemental mapping illustrated the metal signal dispersion of Mn, Ce, and DP (dopants = Co, Ni, Fe, Cu, Cr) in five catalysts (Figure 5) using 9MnO₂–1CeO₂ as the supporting catalyst. Elemental mappings of Co, Ni, Fe, Cu, and Cr revealed that all DPs were successfully and separately doped into their corresponding Mn–Ce catalysts. No obvious aggregations of DP were observed for DP/9MnO₂–1CeO₂; high-angle annular dark-field scanning TEM (HAADF-STEM) images revealed that the mesoporous structure of all catalysts was maintained after loading different transition metals onto the catalyst surface by the wet impregnation method.

DP/9MnO ₂ -1CeO ₂ DP=	Co	Ni	Fe	Cu	Cr
DP					
HAADF					
Mn					
Ce					

Figure 5. TEM images and EDS elemental mapping of DP/9MnO₂–1CeO₂ catalysts.

2.1.4. X-ray Photoelectron Spectroscopy (XPS) Analysis

X-ray photoelectron spectroscopy was used to analyze the surface elemental compositions and oxidation states of catalysts. The Mn 2p and Ce 3d XPS spectra of selected catalysts are presented in Figure 6. Proportions of the surface compositions of the catalysts were calculated from the XPS results and are shown in Table 3. The Mn 2p spectrum (Figure 6a) of all samples, beside 9MnO₂-1CeO₂, can be deconvoluted into three distinguished peaks at 642.3 eV, 643.1 eV, and 644.4 eV (binding energy), which can be ascribed to Mn²⁺, Mn³⁺, and Mn⁴⁺ [27], respectively, confirming the coexistence of three kinds of Mn species. The signal of Mn³⁺ in 9MnO₂-1CeO₂ was not detected, supposing the amount of this oxidation state to be below the detection limit. The ratio of (Mn²⁺ + Mn³⁺)/Mn⁴⁺ increased from 6.3 (9MnO₂-1CeO₂) to 8.1 (Cu/9MnO₂-1CeO₂) and 8.2 (Cu/9MnO₂-1CeO₂), suggesting that the Mn ions obtained electrons in the systems (the valence of partial Mn ions dropped from +4 to +2 and +3) after doping trace Cu and Fe on 9MnO₂-1CeO₂. In the Ce 3d spectra (Figure 6b), the peaks labeled as v, v2, u, and u2 belonged to Ce³⁺, and the v1, v3, v4, and u1, u3, u4 belonged to Ce⁴⁺ [28]. The ratios of Ce³⁺/Ce⁴⁺ decreased from 0.75 to 0.52 after increasing the ceric molar ratio from 10% to 30%, indicating that oxygen vacancy decreased with added amounts of cerium ion. It could be concluded that doping transition metals on 9MnO₂-1CeO₂ resulting in optimal Mn/Ce not only provided more oxygen vacancy by sustaining higher Ce³⁺/Ce⁴⁺ ratio but also promoted catalytic activity by reducing Mn⁴⁺ to Mn²⁺ and Mn³⁺.

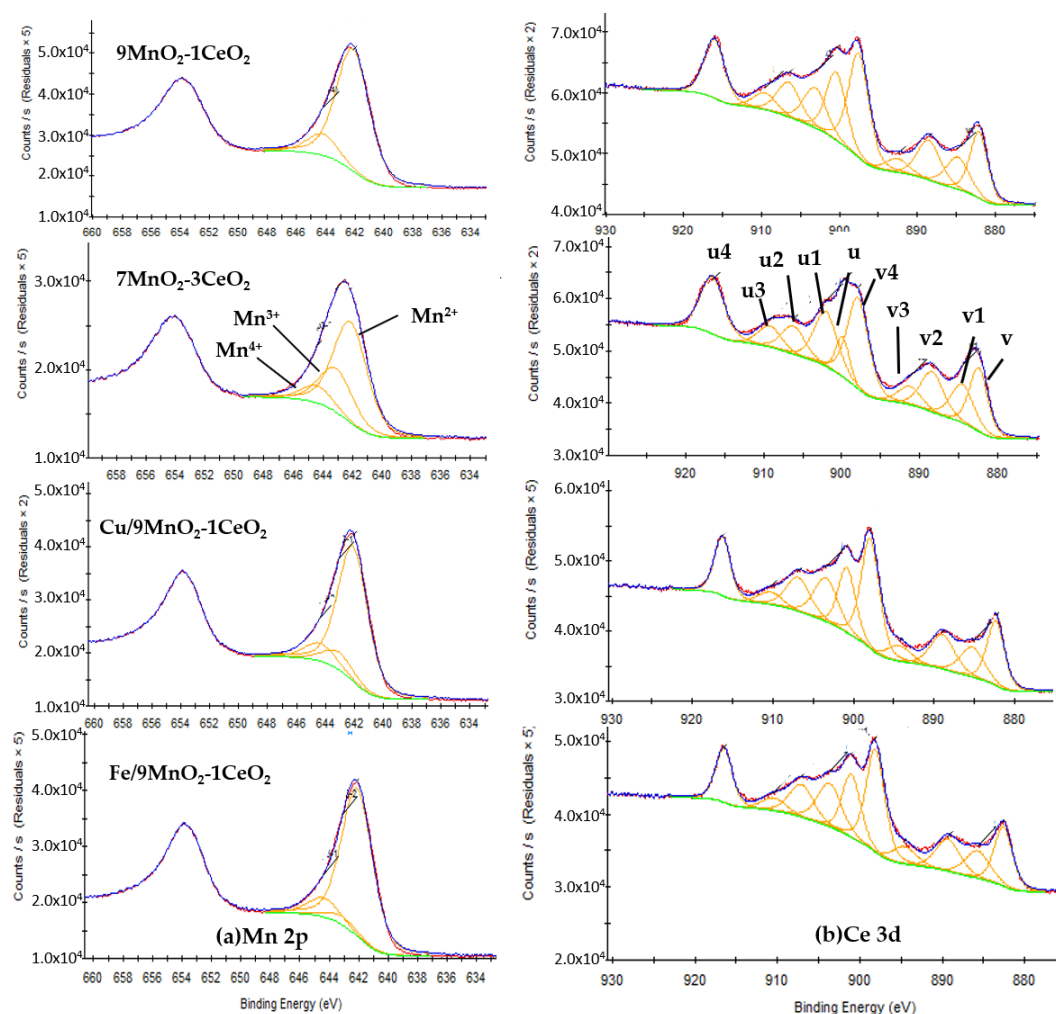


Figure 6. The Mn 2p and Ce 3d XPS spectra of selected catalysts.

Table 3. The Mn 2p and Ce 3d XPS spectra of selected catalysts.

Catalyst	Mn ratio			$(\text{Mn}^{2+} + \text{Mn}^{3+})/\text{Mn}^{4+}$	$\text{Ce}^{3+}/\text{Ce}^{4+}$
	Mn^{2+}	Mn^{3+}	Mn^{4+}		
9MnO ₂ -1CeO ₂	6.32	0	1	6.3	0.75
7MnO ₂ -3CeO ₂	6.17	2.67	1	9.0	0.52
Cu/9MnO ₂ -1CeO ₂	7.18	0.95	1	8.1	0.72
Fe/9MnO ₂ -1CeO ₂	7.90	0.48	1	8.2	0.72

2.2. Catalytic Performance Results

Table 4 presents results on the catalytic activities of different mesoporous catalysts for comparison. All the catalytic materials listed in Table 4 were synthesized by our group for various oxidation catalysis purposes. For NO oxidation in this study, we compared their catalytic effects to verify if the mesoporous mMnO₂-nCeO₂ materials possess the desired catalytic ability for this study. The oxidation process began at room temperature, and the temperature was steadily increased to 200 °C, wherein NO oxidation to NO₂ proceeded in the presence of a catalyst. The temperature of NO_x stream in tail-end flue gas was generally below 200 °C, and the reaction temperature of fast SCR was approximately 200–250 °C; therefore, the temperature of ½-fraction NO oxidation should be lower than 200 °C. A concentration between 200–300 ppm of the NO inlet was maintained in accordance with the typical flue gas concentration range. At 200 °C, MnO₂ and Co₃O₄ oxidized 56.8% and 55.6% of NO into NO₂, respectively. The conversion rates of Pt/Cr₂O₃ and Pt/Fe₂O₃ measured only 29.8% and 35.7%, respectively. These findings agreed with those in the literature [29] on the superior performance of mesoporous MnO₂, particularly 3D-MnO₂, as an oxidation catalyst. Precious metals such as Pt [30] and Rh [31] dispersed on specific metal oxides with a high oxygen storage capacity (e.g., CeO₂ and Fe₂O₃) are highly active for oxidation reaction; however, this study doped Pt in mesoporous Cr₂O₃ and Fe₂O₃ to promote their activity and no reaction of note was observed from Pt/Cr₂O₃ and Pt/Fe₂O₃, which implied that neither of these metal oxides were ideal supporting catalysts of NO oxidation for our purposes. Conversely, the doping of MnO₂ with Rh or Co led to an increase in activity at 200 °C from 56.8% to 59.1% (Rh/MnO₂) and to 61.5% (Co/MnO₂), respectively. The optimal tested catalysts were 9MnO₂-1CeO₂ and 7MnO₂-3CeO₂, which yielded 71.0% and 65.0% of NO converted to NO₂, respectively. Ce was added onto MnO₂ to improve the oxygen storage capacity and oxygen mobility of the catalyst. The Ce addition resulted in a higher activity (71.0%) of 9MnO₂-1CeO₂ compared with that of 7MnO₂-3CeO₂ (65.5%), which indicated that the proper addition of CeO₂ enhanced the metal-support interaction and increased the reducible phase, thus benefitting the reaction. Because Ce mixed with mesoporous MnO₂ catalysts had a higher oxidation ability, the observation of 50% NO oxidation to NO₂ at lower temperatures was expected.

Table 4. Catalytic oxidation activity of various catalysts.

Catalyst	NO Inlet (ppm)	Fraction of NO Converted to NO ₂ @200 °C (%)	Temperature of 50% NO Oxidation to NO ₂ (°C)
Pt/Cr ₂ O ₃	263	29.8	>200
Co ₃ O ₄	260	55.6	190
Pt/Fe ₂ O ₃	250	35.7	>200
MnO ₂	310	56.8	189
Rh/MnO ₂	245	59.1	185
Co/MnO ₂	260	61.5	180
9MnO ₂ -1CeO ₂	266	71.0	167
7MnO ₂ -3CeO ₂	252	65.5	172

Figure 7 presents the NO curve of oxidation against the reaction temperature of 9MnO₂–1CeO₂. NO₂ concentration increased whereas NO concentration decreased with temperature. The ratio of NO:NO₂ reached 1:1 at 167 °C. Although studies have indicated that oxygen from NO, gaseous O₂, and catalyst oxygen all function as oxygen sources for the formation of N₂O [5], the results of Fourier transform infrared (FT-IR) spectroscopy verified that inlet NO was oxidized to NO₂ and no other species were observed. Furthermore, the oxidation of NO to NO₂ by mMnO₂–nCeO₂ avoided the formation of N₂O because of the catalyst's characteristics and the mild reaction conditions. For the same experimental conditions, an equimolar gas of NO and NO₂ over 7MnO₂–3CeO₂ was also observed at 172 °C (Table 4).

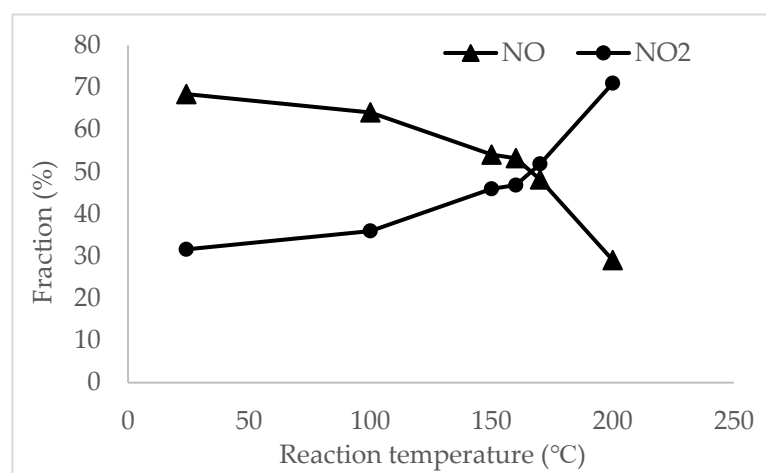


Figure 7. NO oxidation with respect to temperature of 9MnO₂–1CeO₂.

To better evaluate the catalytic activity, kinetic parameters were calculated according to the following equation from the NO_x conversion [32,33].

$$k = -\frac{V}{W} \times \ln(1 - x) \quad (3)$$

where k is the reaction rate coefficient (mL g^{−1} s^{−1}), V is the total gas flow rate (mL s^{−1}), W is the mass of catalysts in the quartz reactor, and x is the conversion of NO to NO₂ in the testing activity. This equation is based on the theory that the reaction is first-order dependent on NO and zero-order dependent on O₂. As shown in Figure 8a, it was observed clearly that the catalytic reaction rate of 9MnO₂–1CeO₂ at high temperature is much greater than that at low temperatures and the rate constant for oxidation of 50% NO to NO₂ at 167 °C was 2.5 mL g^{−1} s^{−1}. The apparent activation energy was calculated using the Arrhenius equation given by

$$k = k_0 e^{-E_a/RT} \quad (4)$$

In Equation (4), E_a is the apparent activation energy. It can be calculated from the slope of the curve $\ln(k)$ versus $1/T$, as shown in Figure 8b. The apparent activation energy of NO oxidation reaction on the 9MnO₂–1CeO₂ was 13.6 kJ/mol, which is lower than that of pure nanorod MnO₂ (E_a = 20.9 kJ/mol) [34], commercial Cu-zeolite (E_a = 29–31 kJ/mol) [35], and Pt/Al₂O₃ (E_a = 39 kJ/mol) [36]. This result was also consistent with that of 9MnO₂–1CeO₂, which oxidized 50% NO to NO₂ at a lower temperature than that of pure MnO₂ (Table 4).

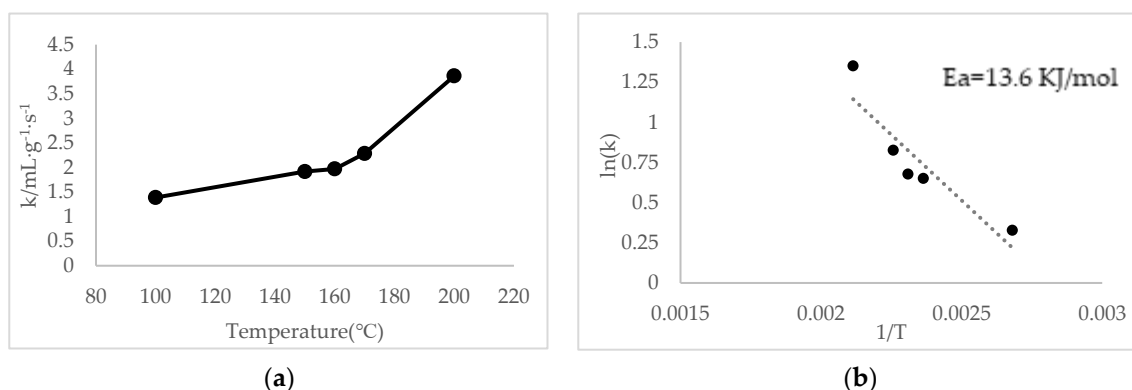


Figure 8. (a) Reaction rate coefficient and (b) Arrhenius plot of $9\text{MnO}_2-1\text{CeO}_2$.

Replacing a small fraction of cations in a supporting metal oxide with a different cation served as a useful strategy for improving catalytic activity. To investigate the effect of transition metal doping on lower catalytic temperature, five transition metals (Co, Ni, Fe, Cu, and Cr) were individually loaded on $9\text{MnO}_2-1\text{CeO}_2$ because of its promising NO oxidation capability and then tested for their catalytic activity based on equimolar oxidation from NO to NO_2 . Metal doping increased low-temperature oxidation activity (Figure 9). The catalytic activity test indicated that all doped $9\text{MnO}_2-1\text{CeO}_2$ exhibited enhanced NO oxidation activity. When $9\text{MnO}_2-1\text{CeO}_2$ was doped by transition metals, the fraction of NO converted to NO_2 at 200°C increased from 71.0% to 79.7% (Co/ $9\text{MnO}_2-1\text{CeO}_2$), 80.0% (Ni/ $9\text{MnO}_2-1\text{CeO}_2$), 78.7% (Fe/ $9\text{MnO}_2-1\text{CeO}_2$), 81.0% (Cu/ $9\text{MnO}_2-1\text{CeO}_2$), and 75.0% (Cr/ $9\text{MnO}_2-1\text{CeO}_2$)—that is, 50% NO oxidation to NO_2 occurred at a lower temperature compared with pristine $9\text{MnO}_2-1\text{CeO}_2$. Among the transition metals, Cu, Ni, Co, Fe, and Cr exhibited the highest to lowest oxidation activity, respectively; all transition metals had higher oxidation activity levels than pristine $9\text{MnO}_2-1\text{CeO}_2$. Cu exhibited the highest activity among all five doped mesoporous $9\text{MnO}_2-1\text{CeO}_2$ and increased NO oxidation activity by 20% at 200°C compared with pristine $9\text{MnO}_2-1\text{CeO}_2$. This finding agreed with those of a previous study [16] in which density functional theory calculations indicated that Cu doping may facilitate the formation of oxygen vacancies in MnO_2 more effectively than in Fe, Co, and Ni doping. In addition, all doped mesoporous $9\text{MnO}_2-1\text{CeO}_2$ exhibited higher NO oxidation activity than pristine $9\text{MnO}_2-1\text{CeO}_2$, demonstrating that metal doping constitutes a feasible method of increasing the catalytic activity of $9\text{MnO}_2-1\text{CeO}_2$.

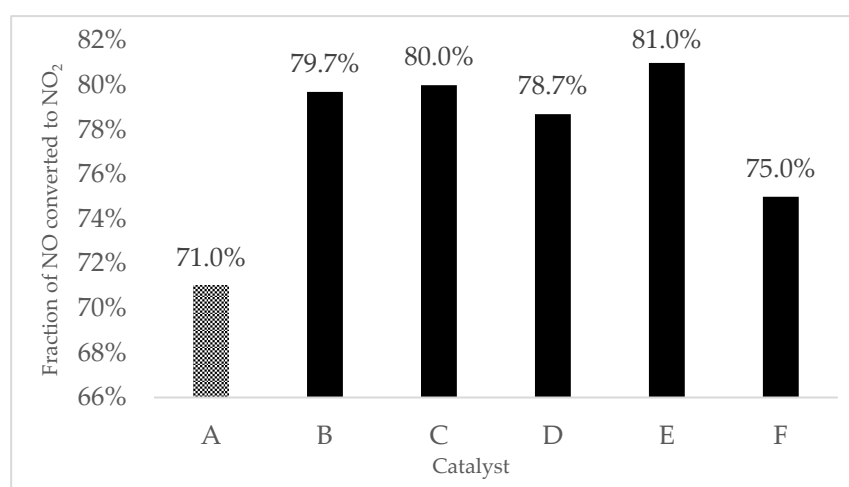


Figure 9. Catalytic performance for NO oxidation to NO_2 at 200°C : (A) $9\text{MnO}_2-1\text{CeO}_2$, (B) Co/ $9\text{MnO}_2-1\text{CeO}_2$, (C) Ni/ $9\text{MnO}_2-1\text{CeO}_2$, (D) Fe/ $9\text{MnO}_2-1\text{CeO}_2$, (E) Cu/ $9\text{MnO}_2-1\text{CeO}_2$, and (F) Cr/ $9\text{MnO}_2-1\text{CeO}_2$.

Figure 10 indicates that the reaction temperature of NO:NO₂ reached 1:1 for doped and pristine 9MnO₂–1CeO₂. As in Figure 9, Cu/9MnO₂–1CeO₂ exhibited the best catalytic activity and achieved equimolar NO:NO₂ at 140 °C. Although Fe/9MnO₂–1CeO₂ had lower NO oxidation activity compared with Ni/9MnO₂–1CeO₂ and Co/9MnO₂–1CeO₂ at 200 °C, Fe/9MnO₂–1CeO₂ and Cu/9MnO₂–1CeO₂ both exhibited better equimolar NO:NO₂ performance at 140 °C. Figure 10 also indicates that all doped mesoporous 9MnO₂–1CeO₂ had a lower reaction temperature of equimolar NO and NO₂ compared with pristine 9MnO₂–1CeO₂.

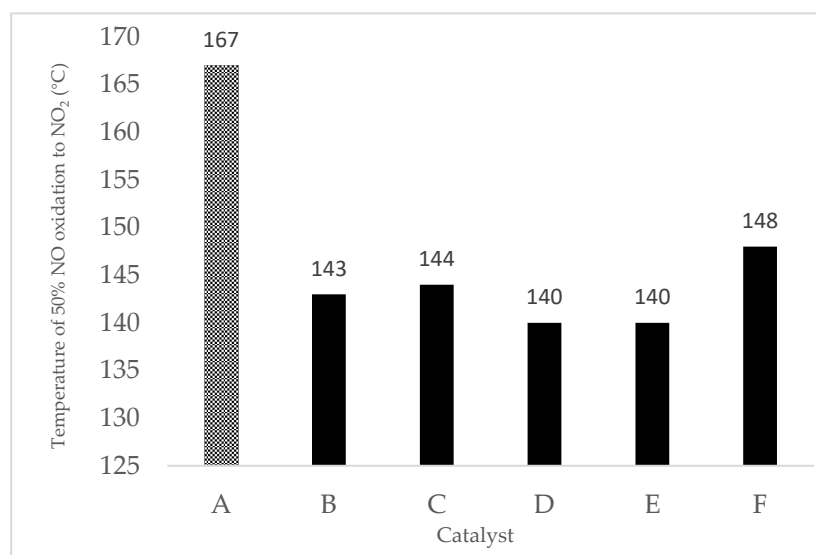


Figure 10. Reaction temperature for oxidation of 50% NO to NO₂: (A) 9MnO₂–1CeO₂, (B) Co/9MnO₂–1CeO₂, (C) Ni/9MnO₂–1CeO₂, (D) Fe/9MnO₂–1CeO₂, (E) Cu/9MnO₂–1CeO₂, and (F) Cr/9MnO₂–1CeO₂.

Because 9MnO₂–1CeO₂ exhibited higher catalytic activity than other compounds in Table 4 and its Fe- and Cu-doped species revealed the most promising NO oxidation activity, the effects of Fe- and Cu-doped 7MnO₂–3CeO₂ on equimolar catalysis of NO and NO₂ were further studied (Table 5). Although 9MnO₂–1CeO₂ converted a higher fraction of NO to NO₂ at 200 °C and had better oxidation activity, no obvious difference in reaction temperature for 50% NO oxidation to NO₂ was found after doping Cu and Fe.

Table 5. Catalytic NO oxidation activity of selected DP/mMnO₂–nCeO₂ catalysts.

Catalyst	Fraction of NO Converted to NO ₂ @200 °C (%)	Temperature of 50% NO Oxidation to NO ₂ (°C)
9MnO ₂ –1CeO ₂	71.0	167
7MnO ₂ –3CeO ₂	65.5	172
Fe/9MnO ₂ –1CeO ₂	78.7	140
Fe/7MnO ₂ –3CeO ₂	82.0	140
Cu/9MnO ₂ –1CeO ₂	81.0	140
Cu/7MnO ₂ –3CeO ₂	78.0	138

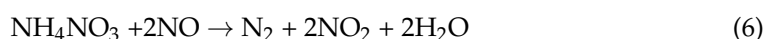
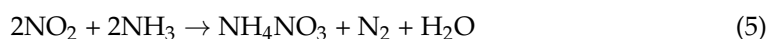
Studies have indicated that Al₂O₃ is an ideal support for NO catalytic oxidation because of its thermal stability [37]; perovskite-type oxides are another group of promising catalysts for NO oxidation due to their low cost, good activity, and thermal stability [38,39]. Al₂O₃ doped with several precious metals and perovskite-type catalysts was studied to compare their NO oxidation activity with those of DP/mMnO₂–nCeO₂ in this present study (Table 6). The data revealed that DP/mMnO₂–nCeO₂ still converted 50% NO to NO₂ with the highest level of energy efficiency.

Table 6. Properties of metal-oxide- and perovskite-type catalysts for NO oxidation.

Catalyst	Fraction of NO Converted to NO ₂ @200 °C (%)	Temperature of 50% NO Oxidation to NO ₂ (°C)	Refs.
DP/mMnO ₂ -nCeO ₂ (m:n = 9:1 and 7:3)	75~81%	140~200	This work
Pt/Al ₂ O ₃	40%	250	[40]
La _{1-x} Ce _x CoO ₃	5%	270	[41]
Pt-Pd/Al ₂ O ₃	10%	>400	[42]
Mn-Ce/γ-Al ₂ O ₃	40%	225	[43]
Co ₃ O ₄ -CeO ₂	20%	230	[44]

2.3. Mechanisms of NO Oxidation and Fast SCR

The fast SCR reaction has a smaller activation energy (≈ 38 kJ/mol) compared with the standard SCR reaction (≈ 64 kJ/mol). This resulted in a reaction rate difference between the two reactions with a factor of ≈ 10 at 200 °C. The fast SCR reaction is derived from two equations involving NH₄NO₃, an intermediate from NH₃, as depicted in reactions (5) and (6). NO₂ is a critical component of fast SCR. As mentioned, the oxidation of NO plays a vital role in fast SCR.



Tang et al. [45] studied the mechanism of NO catalytic oxidation over MnO_x. The most likely process of NO oxidation to NO₂ over MnO_x was described as the following: first, NO was absorbed on Mn sites and the resulting nitrosyls (M–N=O) were oxidized to form nitrates (NO₃[−]); finally, the product NO₂ was formed and released after the decomposition of nitrates. Zhong et al. [46] also proposed the possible reaction pathways of NO oxidation on Ce sites. An oxygen vacancy on Ce could bond O₂ to form superoxide radicals (O₂[−]), resulting in the formation of free nitrates due to the strong interaction between O₂[−] and NO. In addition, the oxygen vacancy could be recovered by Ce sites after the release of NO₂. Our study results agree with these findings; we adopted a mixture of Mn and Ce oxides as supporting catalysts and used doped transition metals to lower the oxidation temperature of converting 50% NO oxidation to NO₂.

3. Materials and Methods

3.1. Materials

Analytical grade metal precursor chemicals and organic solvents were purchased from Sigma–Aldrich (St. Louis, MO, USA), Thermo Scientific (Waltham, MA, USA), and Alfa Chemicals (Binfield, Bracknell Forest, UK). Deionized (DI) water was used as the solvent in all experiments. All chemicals and reagents were used directly as received without further purification.

3.2. Preparation

3.2.1. Mn–Ce Catalyst Preparation

9MnO₂–1CeO₂

The 9MnO₂–1CeO₂ catalyst was prepared using two solvent methods. First, 4.67 g (18.6 mmol) of Mn(NO₃)₂·4H₂O (MW = 251.01) and 0.90 g (2.07 mmol) of Ce(NO₃)₃·6H₂O (MW = 434.22) were dissolved in 10.24 mL of DI to form a Mn salt and Ce salt solution. Second, 5.12 g of the mesoporous KIT-6 template (synthesis method [47]) was dispersed in 64 mL of toluene and stirred completely to form a KIT-6 dispersion. Next, the KIT-6 dispersion was added to the Mn salt and Ce salt solution. The mixed solution was heated at 65 °C and slowly stirred to volatilize the water and toluene until a powder formed; the powder was then calcined at 300 °C for 3 h to form MnO₂–CeO₂ (9:1) inside the mesopores.

of the KIT-6 template. Subsequently, the $\text{MnO}_2\text{-CeO}_2$ containing the mesoporous KIT-6 template was dispersed in 2 M $\text{NaOH}_{(\text{aq})}$ and heated to 65 °C with stirring for 30 min to remove the KIT-6 template. The product was collected by filtration and repeated washing with DI until a pH of 7 was achieved. Finally, the mesoporous metal oxide $\text{MnO}_2\text{-CeO}_2$ (9:1) was procured after drying at 80 °C for 12 h. The EDS results in atomic percentages are as follows: C (7.17), O (40.18), Na (1.22), Si (0.57), Mn (45.52), and Ce (5.34).

7MnO₂-3CeO₂

Similar in preparation to 9MnO₂-1CeO₂, the only difference was the adjustment of the molar ratio of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to 7:3. The EDS results in atomic percentages are as follows: C (7.83), O (54.65), Na (2.47), Si (2.95), Mn (22.28), and Ce (9.82).

3.2.2. DP-Mn-Ce Catalyst Preparation (DP = Fe, Co, Ni, Cu, or Cr)

Co/9MnO₂-1CeO₂

The Co-Mn-Ce catalysts with 9MnO₂-1CeO₂ were prepared by the wet impregnation method. The reactant molar ratio of Co:(Mn + Ce) was 1:100. A total 2.01 g (21.0 mmol) of 9MnO₂-1CeO₂ was dispersed in 40 mL of methanol. Subsequently, 0.063 g (0.21 mmol) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (MW = 291.03) was dissolved in 20 mL of DI, then poured slowly into the 9MnO₂-1CeO₂ dispersion with stirring to form a mixed solution of cobalt salt/9MnO₂-1CeO₂. Then, 0.08 g of NaBH_4 was dissolved in 20 mL of DI and slowly added to the cobalt salt/9MnO₂-1CeO₂ solution and the mixture solution was stirred for another hour. The product was collected by filtration and alternate washing with DI and ethanol until a pH of 7 was achieved. Finally, the Co/9MnO₂-1CeO₂ was procured after drying at 80 °C for 12 h.

DP/9MnO₂-1CeO₂ and DP/7MnO₂-3CeO₂ (DP = Fe, Ni, Cu, or Cr)

Similar in preparation to Co/9MnO₂-1CeO₂, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were individually loaded on the mMnO₂-nCeO₂ catalysts as dopants.

3.2.3. Preparation of Catalysts for Comparison between them in NO Oxidation Performance

Cr₂O₃, Co₃O₄, Fe₂O₃, and MnO₂

Porous catalysts Cr₂O₃, Co₃O₄, Fe₂O₃, [48] and MnO₂ were synthesized following the same method of preparation for the Mn-Ce-catalysts; 8.28 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 6.02 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 8.36 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used, respectively.

Pt/Cr₂O₃, Pt/Fe₂O₃, Rh/MnO₂, and Co/MnO₂

Similar in preparation to Co/9MnO₂-1CeO₂, 0.086 g of H_2PtCl_6 + 3.19 g of Cr₂O₃, 0.086 g of H_2PtCl_6 + 3.3535 g of Fe₂O₃, 0.0607 g of $\text{Rh}(\text{NO}_3)_3$ + 1.8257 g of MnO₂, and 0.063 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ + 1.8257 g of MnO₂ were used, respectively.

3.3. Catalytic Performance: NO Oxidation to NO₂

The measurement of the oxidation activity from NO to NO₂ was conducted in a fixed-bed continuous flow quartz reactor with an internal diameter of 4.9 mm by temperature-programmed reaction technique. A thermocouple was placed in the region of the catalyst bed to monitor the reaction temperature; the temperature, which was monitored by a proportional-integral-derivative controller, was raised from room temperature to 200 °C. A 2 cm high (0.374 cm³) sample, which was pressed into blocks and sieved with 30 mesh, was used for the NO oxidation test. The mixed reactant gas contained the following constituents: 50 mL/min of 1000 ppm NO, 10 mL/min of 99.9% O₂, and balanced N₂; the total flow rate was 167 mL/min, resulting in a gas hourly space velocity of 26,791. All the catalysts were kept on stream at the target temperature for at least 30 min. The concentration of the outlet gas was measured online by an FT-IR spectrometer (Work IR-104, ABB Bomem, QC, Canada) with self-developed software. The method developed

allowed the simultaneous determination of NO, NO₂, N₂O, and other related gases if required. The NO oxidation fraction was calculated according to the following formula: NO oxidation (%) = ([NO₂]_{out}/([NO]_{out}+ [NO₂]_{out}) × 100%, with the subscripts “out” indicating the outlet concentration at a steady state. The concentrations of the feed and the output gases were calculated from the relative peak areas of all identified gases with respect to the internal N₂ standard.

4. Conclusions

This study synthesized a series of 3D-ordered mesoporous metal oxides DP/mMnO₂-nCeO₂ (m:n = 9:1 and 7:3) with doped metals (DP) Fe, Co, Ni, Cu, and Cr. These catalysts functioned as pre-oxidation catalysts for SCR to convert 50% NO to NO₂ at 140–200 °C and lowered the SCR reaction temperature to 200 °C.

All doped mesoporous mMnO₂-nCeO₂ had a lower reaction temperature for equimolar NO:NO₂ compared with the corresponding pristine mMnO₂-nCeO₂. Among them, Cu/mMnO₂-nCeO₂ and Fe/mMnO₂-nCeO₂ exhibited the best catalytic activity and achieved equimolar NO:NO₂ at as low as 138–140 °C. These findings provide a feasible solution for modifying the flue gas treatment system from high-dust SCR to tail-end SCR, resulting in eventual energy savings, lower catalyst cost, and prolonged catalyst life.

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