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Catalytic Elimination of Carbon Monoxide, Ethyl Acetate, and Toluene over the Ni/OMS-2 Catalysts

Ning Dong ¹, Mengyue Chen ¹, Qing Ye ^{1,*} , Dan Zhang ¹ and Hongxing Dai ^{2,*}

¹ Key Laboratory of Beijing on Regional Air Pollution Control, Department of Environmental Science, Faculty of Environment and Life, School of Environmental and Chemical Engineering, Beijing University of Technology, Beijing 100124, China; dongning@emails.bjut.edu.cn (N.D.); chenmy@emails.bjut.edu.cn (M.C.); zhangdan@emails.bjut.edu.cn (D.Z.)

² Beijing Key Laboratory for Green Catalysis and Separation, Key Laboratory of Beijing on Regional Air Pollution Control, Key Laboratory of Advanced Functional Materials, Education Ministry of China, and Laboratory of Catalysis Chemistry and Nanoscience, Department of Environmental Chemical Engineering, School of Environmental and Chemical Engineering, Faculty of Environment and Life, Beijing University of Technology, Beijing 100124, China

* Correspondence: yeqing@bjut.edu.cn (Q.Y.); hxdai@bjut.edu.cn (H.D.); Tel.: +86-10-6739-1659 (Q.Y.); +86-10-6739-6118 (H.D.); Fax: +86-10-6739-1983 (Q.Y.); +86-10-6739-1983 (H.D.)

Abstract: The Ni-loaded cryptomelane-type manganese oxide octahedral molecular sieve (OMS-2) catalysts ($x\text{Ni}/\text{OMS-2}$: $x = 1, 3, 5$, and $10 \text{ wt\%}$) were prepared by a pre-incorporation method. Physicochemical properties of the as-synthesized materials were characterized by means of various techniques, and their catalytic activities for CO, ethyl acetate, and toluene oxidation were evaluated. The loading of Ni played an important role in improving physicochemical properties of OMS-2. Among all of the samples, $5\text{Ni}/\text{OMS-2}$ exhibited the best catalytic activity, with the T_{90} being 155°C for CO oxidation at a space velocity (SV) of $60,000 \text{ mL}/(\text{g}\cdot\text{h})$, 225°C for ethyl acetate oxidation at an SV of $240,000 \text{ mL}/(\text{g}\cdot\text{h})$, and 300°C for toluene oxidation at an SV of $240,000 \text{ mL}/(\text{g}\cdot\text{h})$, which was due to its high Mn^{3+} content and O_{ads} concentration, good low-temperature reducibility and lattice oxygen mobility, and strong interaction between the Ni species and the OMS-2 support. In addition, catalytic mechanisms of the oxidation of three pollutants over $5\text{Ni}/\text{OMS-2}$ were also studied. The oxidation of CO, ethyl acetate, and toluene over the catalysts took place first via the activated adsorption, then intermediates formation, and finally complete conversion of the formed intermediates to CO_2 and H_2O .

Keywords: cryptomelane-type manganese oxide octahedral molecular sieve; supported nickel catalyst; CO oxidation; ethyl acetate oxidation; toluene oxidation



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1. Introduction

CO and volatile organic compounds (VOCs) bring about great harmfulness to human health and the atmosphere [1]. They come from a variety of sources, such as industrial production, vehicle emissions, and human activities [2]. Therefore, effective removal of CO and VOCs is an urgent task. In the past decades, extensive research has been conducted to eliminate these harmful pollutants from the environment. The use of catalytic oxidation to treat CO and VOCs is one of the most effective technologies [3]. In this process, CO and VOCs are completely converted into CO_2 and/or H_2O over the supported noble metal and transition metal catalysts without the generation of other products. Catalytic oxidation possesses the advantages of low energy consumption, no secondary pollution, good safety, and wide applications, in particular, supported noble metal catalysts show high efficiency in CO and VOCs elimination at low temperatures [4]. However, the scarcity of resources and the high price impose limitations on the wide application of such materials [5]. Due to the advantages of low cost and good catalytic performance, transition metal oxides are

often used to catalyze the oxidation of pollutants. Hence, they have gained much attention in the removal of CO and VOCs.

It has been known that manganese oxide-supported transition metals with excellent catalytic activity tend to perform well in the oxidation of CO and VOCs. Transition metal modification can improve the catalytic activity of layered birnessite manganese oxide due to the synergistic action of transition metal and manganese oxide. According to a report by Yang et al. [6], who used the high-temperature spontaneous redox method to prepare the $\text{Mn}_3\text{O}_4\text{-NiO-Ni/CNTs}$ catalysts, benzaldehyde could be removed over these materials. After investigating the oxidation of *o*-xylene over $\text{Ag/NiO}_x\text{-MnO}_2$ prepared by the redox and deposition precipitation methods, Wu et al. [7] concluded that good gaseous oxygen activation ability, oxygen bulk mobility, and low-temperature reducibility were the inherent reasons for the high activity of $\text{Ag/NiO}_x\text{-MnO}_2$. Guo et al. [8] synthesized the porous Mn-Ni composite oxide catalysts via an oxalate route and found that they could effectively catalyze the degradation of benzene at low temperatures, which was related to the good low-temperature reducibility, high oxygen mobility, and large surface areas. Dong et al. [9] studied the metal-doped $\alpha\text{-MnO}_2$ catalysts for the combustion of toluene and observed that catalytic oxidation temperature of the Ni-MnO₂ catalyst achieving 90% conversion was 199 °C, and the remarkable low-temperature performance indicated that Ni doping could improve the activity of $\alpha\text{-MnO}_2$. It was also reported that the doping of Ni to the manganese oxide framework improved the reducibility, oxygen migration, and thermal stability and hence enhanced its catalytic performance for toluene oxidation.

The chemical formula of manganese oxide octahedral molecular sieve (OMS-2) composed of octahedron $[\text{MnO}_6]$ is $\text{KMn}_8\text{O}_{16} \cdot n\text{H}_2\text{O}$ [10]. The octahedral $[\text{MnO}_6]$ chain of its structure is connected by oxygen atoms at the vertex of the octahedron, forming a tunnel structure with a diameter of $0.46 \text{ nm} \times 0.46 \text{ nm}$ [11]. The K^+ and H_2O in the channels play a role in maintaining charge balance and structural stability. The OMS-2 possesses a variety of manganese ions with different valences (Mn^{2+} , Mn^{3+} , and Mn^{4+}) [12], a large number of open interlayer pore structures, and abundant surface hydroxyl groups. Therefore, it shows strong ion exchange ability, large adsorption capacity, and excellent catalytic performance. It has been demonstrated that the OMS-2 modified by a transition metal can improve its physicochemical property and catalytic activity.

In this study, we report the preparation of a series of Ni/OMS-2 catalysts, their physicochemical properties, and their catalytic activities for the oxidation of CO, ethyl acetate, and toluene. The results showed that the loading of Ni could modify the physicochemical property and catalytic activity of OMS-2 due to the strong synergistic action of Ni and manganese oxide.

2. Experimental

2.1. Catalyst Preparation

The OMS-2 support was prepared by adopting the buffer solution method. In a typical preparation procedure, manganese acetate (11.0 g) was dissolved in deionized water (DW). Dissolve potassium acetate with DW to obtain a buffer solution. Then, under magnetic stirring, an aqueous solution of potassium permanganate (6.5 g) was slowly added to the mixed solution of manganese acetate. The product was obtained after refluxing the above solution at 100 °C for 20 h, followed by suction filtration and washing several times with DW until a neutral pH was reached. Finally, the wet solid was dried at 105 °C overnight and calcined at 400 °C for 4 h in a muffle furnace, thus obtaining the OMS-2 support.

The $x\text{Ni/OMS-2}$ (the x was the mass percentage of Ni) samples were prepared using the pre-incorporation method. In a typical process, manganese acetate (11.0 g) in DW was dissolved in pre-composited buffer solution composed of potassium acetate and acetic acid. Then, an aqueous solution of nickel nitrate (Ni loading = 1, 3, 5, and 10 wt%) and potassium permanganate was added slowly under stirring. The product was obtained after refluxing the above solution at 100 °C for 20 h, followed by suction filtration and washing several times with DW until a neutral pH was achieved. The wet solid was placed in an

oven and dried at 105 °C overnight. Finally, the dried sample was calcined in a muffle furnace at 400 °C for 4 h, thus generating the $x\text{Ni}/\text{OMS-2}$ ($x = 1, 3, 5$, and 10 wt%) samples.

2.2. Catalyst Characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8-Advance diffractometer in the 2θ range of 5–80° with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm), in which the operating voltage and current were 50 kV and 30 mA, respectively. Fourier transform infrared (FT-IR) spectra of the samples were measured on a Thermo Scientific Nicolet 6700 FTIR spectrometer in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} . Morphologies of the samples were observed on a S-4300 scanning electron microscope (SEM, Japan Hitachi) with an SE probe. Surface areas of the samples were calculated using the Brunauer-Emmett-Teller (BET) equation, and their pore-size distributions were determined using the Barrett-Joyner-Halenda (BJH) method according to the desorption branch data of the isotherms. The thermogravimetry (TG) test was carried out on a microcomputer-differential thermal balance of Beijing Hengjiu Scientific Instrument Factory. The samples were dried at 120 °C for 2 h and kept in an N_2 flow of 60 mL/min at 25 °C for 50 min. The linear heating rate was 10 °C/min, and the test temperature range was 25–900 °C. X-ray photoelectron spectroscopic (XPS) spectra of the samples were recorded on an ESCALAB 250 XI spectrometer using Al $K\alpha$ as an excitation source. The Mn 2p, O 1s, and Ni 2p binding energies of the samples were calibrated against the C 1s signal at BE = 284.6 eV of the contaminant carbon. Oxygen temperature-programmed desorption (O_2 -TPD) of the samples was conducted on a Builder PCA-1200 analyzer. The sample (100 mg) was pretreated at 400 °C and saturated in a 10 vol% O_2/He flow of 30 mL/min at 100 °C. After being purged with pure He (30 mL/min) at 100 °C for 1 h, O_2 desorption took place at a ramp of 10 °C/min in a He flow of 30 mL/min from 30 to 850 °C. H_2 temperature-programmed reduction (H_2 -TPR) of the samples was performed on a Builder PCA-1200 analyzer. Before H_2 -TPR experiment, 100 mg of the sample was pretreated in a 5 vol% O_2/N_2 flow of 30 mL/min at 400 °C for 1 h and subsequently cooled to room temperature. The sample was then reduced in a 5 vol% H_2/N_2 flow of 30 mL/min at a ramp of 10 °C/min from room temperature to 1000 °C. The reduction peaks were calibrated against the complete reduction data of a standard powdered CuO. The in situ diffuse reflectance infrared spectroscopic (DRIFTS) experiments were carried out on a Bruker TENSOR II spectrometer characterized by a reaction chamber that could withstand high temperatures (Harrick Praying Mantis). The sample was packed in the sample cup of the reaction chamber and heated to 400 °C at a total N_2 flow of 200 mL/min for 1 h in order to remove any adsorbed impurities. Each spectrum had a resolution of 4 cm^{-1} with 32 accumulated scans.

2.3. Catalytic Activity Evaluation

Catalytic activities of the samples for CO, ethyl acetate, and toluene oxidation were evaluated in a fixed-bed quartz tube reactor, in which 50 mg (40–60 mesh) of the sample was mixed with 150 mg of quartz sands (40–60 mesh). (i) For CO oxidation, a 1.08 vol% CO/air (balance) gas mixture was used, and the total flow rate was 50 mL/min (giving a space velocity (SV) of 60,000 $\text{mL}/(\text{g}\cdot\text{h})$), and the CO concentrations in the outlet of the reactor were analyzed online by a gas chromatograph (GC-14C, Shimadzu) with a thermal conductivity detector (TCD). (ii) For ethyl acetate and toluene oxidation, 2000 ppm ethyl acetate or toluene generated by N_2 bubbling was mixed with an airflow (the total flow rate = 200 mL/min), the SV was 240,000 $\text{mL}/(\text{g}\cdot\text{h})$, and the reaction products were analyzed online by a gas chromatograph (GC-7900, Techcomp) equipped with a flame ion detector (FID) for organics analysis. The conversion of CO, ethyl acetate, or toluene was defined according to the equation of $(C_{\text{in}} - C_{\text{out}})/C_{\text{in}} \times 100\%$, where C_{in} and C_{out} represent the CO, ethyl acetate, or toluene inlet and outlet concentrations, respectively.

3. Results and Discussion

3.1. XRD Analysis

XRD patterns of the OMS-2 and x Ni/OMS-2 samples are shown in Figure 1. The characteristic diffraction peaks of each x Ni/OMS-2 were consistent with those of OMS-2, indicating formation of a typical tetragonal cryptomelane structure (JCPDS PDF# 42-1348). In other words, the crystal structure of OMS-2 was not altered after Ni loading. The diffraction peaks at $2\theta = 12.7^\circ, 17.9^\circ, 26.3^\circ, 28.8^\circ, 37.7^\circ, 42.1^\circ, 49.9^\circ, 51.9^\circ$, and 60.1° , corresponding to the (110), (200), (220), (310), (211), (301), (411), (600), and (521) crystal planes of the cryptomelane structure, respectively [13]. Compared with the characteristic diffraction peak intensity of OMS-2, that of the x Ni/OMS-2 samples was weakened, which was related to the decrease in crystallinity of the sample after Ni loading. This result might be caused by the partial replacement of K by Ni in the 2×2 channel when Ni and K co-existed during the sample preparation process [14]. Compared with the characteristic angles in the diffraction peak of OMS-2, those of the x Ni/OMS-2 samples were slightly shifted to higher angles. The possible reason was that the relatively small Ni ions (48–69 pm in size) replaced a part of the big Mn ions (53–67 pm in size) in the $[\text{MnO}_6]$ octahedron during the sample preparation process. Ni and Mn interacted to form the Ni–O–Mn bonds via the O atoms, and the interaction between Ni and Mn pulled the crystal into a tighter structure, causing the crystal lattice to decrease. Furthermore, no characteristic diffraction signals due to the crystalline Ni or nickel oxide phase were detected, indicating that Ni was highly uniformly dispersed in the structure of OMS-2.

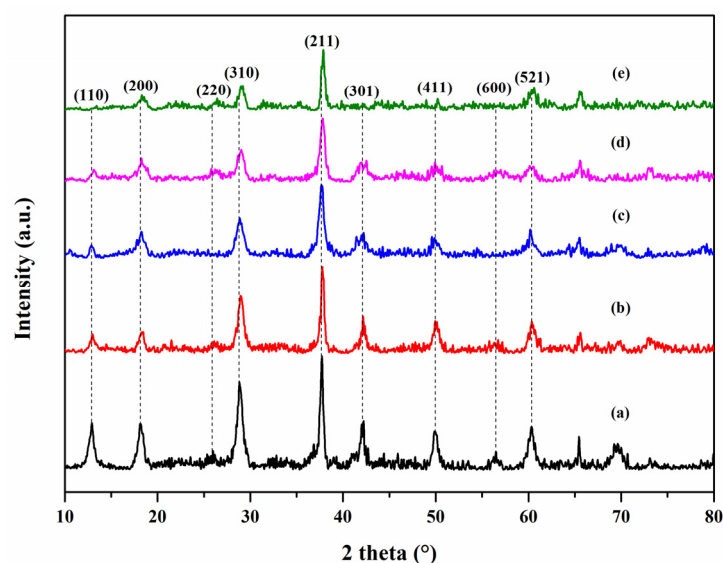


Figure 1. XRD patterns of (a) OMS-2, (b) 1Ni/OMS-2, (c) 3Ni/OMS-2, (d) 5Ni/OMS-2, and (e) 10Ni/OMS-2.

3.2. FT-IR Analysis

Figure 2 depicts the FT-IR spectra of all the samples. The characteristic absorption bands of all the samples were similar and in the range of $4000\text{--}400\text{ cm}^{-1}$, indicating that the structure of the OMS-2 support was not damaged after Ni loading, which was in good agreement with the XRD results. The absorption bands at $710, 600, 520$, and 460 cm^{-1} were related to the lattice vibration modes of Mn–O in the $[\text{MnO}_6]$ octahedron [15]. With a rise in Ni loading, intensity of these absorption bands decreased gradually, which might be caused by the fact that the Ni loading changed the environment of the 2×2 channels, thereby influencing the vibration of Mn–O. After Ni loading, the vibration absorption superposition of the Ni–O–Mn bonds increased the intensity of the absorption band at 710 cm^{-1} of the x Ni/OMS-2 samples, which was consistent with the formation of the Ni–O–Mn bonds revealed in the XRD investigations. The intensity of the absorption band

at 3400 and 1620 cm^{-1} was attributed to the vibrations of the hydroxyl and water molecules, respectively. Compared with the OMS-2 support, the intensity of the absorption band at 3400 and 1620 cm^{-1} of the $x\text{Ni}/\text{OMS-2}$ samples became intense, indicating that Ni loading enhanced the adsorption of hydroxyl and water molecules. The possible reason was that during the Ni loading process, a more amount of surface defects was generated on the surface of the sample, hence providing a more amount of adsorption sites for hydroxyl and water molecules.

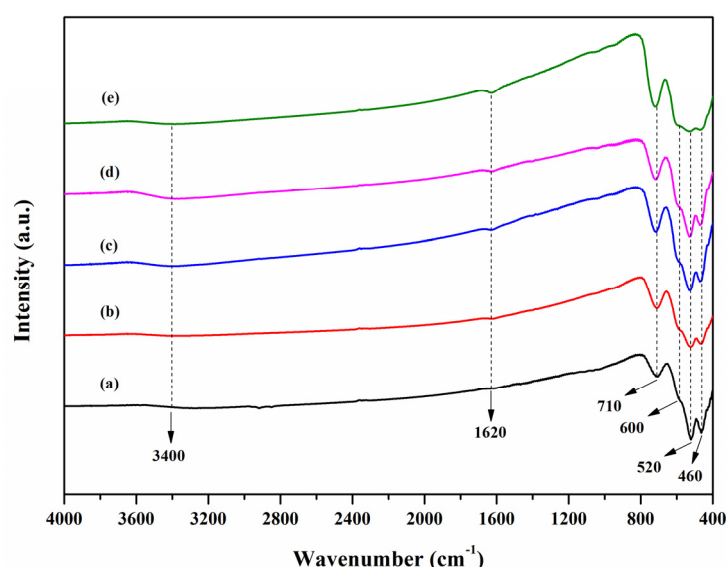


Figure 2. FT-IR spectra of (a) OMS-2, (b) 1Ni/OMS-2, (c) 3Ni/OMS-2, (d) 5Ni/OMS-2, and (e) 10Ni/OMS-2.

3.3. N_2 Adsorption–Desorption Analysis

N_2 adsorption–desorption isotherms of all the samples are illustrated in Figure 3. In the range of $p/p_0 = 0\text{--}0.8$, the appearance of a type I isotherm means that each sample possessed a microporous structure. When p/p_0 was higher than 0.8, the recording of a IV-type isotherm and an H3-type hysteresis loop indicates that all of the samples displayed a slit-like mesoporous structure [16]. Surface area was sorted as 1Ni/OMS-2 ($78.9\text{ m}^2/\text{g}$) > 3Ni/OMS-2 ($72.4\text{ m}^2/\text{g}$) > 5Ni/OMS-2 ($71.2\text{ m}^2/\text{g}$) > 10Ni/OMS-2 ($65.3\text{ m}^2/\text{g}$) > OMS-2 ($51.6\text{ m}^2/\text{g}$). This was not consistent with their catalytic activity order. That is to say, the surface area of the sample was not the key factor influencing its catalytic activity. The surface areas of $x\text{Ni}/\text{OMS-2}$ were higher than that of OMS-2, indicating that Ni loading exerted a significant effect on the structure of OMS-2, as revealed in the XRD and FT-IR analysis results (the changed pore environment, formed Ni–O–Mn bridge oxygen bond, and generated surface defects).

3.4. SEM Analysis

Figure 4a shows that the OMS-2 material displayed a uniform and slender nanofiber-like structure [17], and the average lengths of the nanorods were tens to hundreds of nanometers. As shown in Figure 4b, the nanofibrous structure of the 5Ni/OMS-2 sample became thinner and shorter. The reason for this shortening might be that the loading of Ni suppressed the nanofibrous particles, and the possible reason for the thinning of the nanorods was that Ni replaced part of the K and Mn in the channel, resulting in the reduction in framework and crystal lattice, as confirmed by the XRD and FT-IR results.

3.5. TG Analysis

Figure 5 illustrates the TG/DTG plots of the samples, and detailed weight loss data are summarized in Table 1. The thermal weight loss process of the OMS-2 sample was

roughly divided into four steps at 40–250, 250–550, 550–700, and 700–850 °C. The first step (40–250 °C) showed a weight loss of 1.56 wt%, owing to the physically and chemically adsorbed water. The second step (250–550 °C) exhibited a weight loss of 1.09 wt%, which was associated with the escape of surface oxygen species and part of the lattice oxygen of OMS-2. The third step (550–700 °C) with a weight loss of 3.69 wt% was attributed to the release of lattice oxygen from MnO_2 to Mn_2O_3 [18]. The fourth step (700–850 °C) with a weight loss of 3.27 wt% was attributed to the release of lattice oxygen [19]. The thermal stability test results demonstrate that each sample contained a large amount of mobile lattice oxygen species.

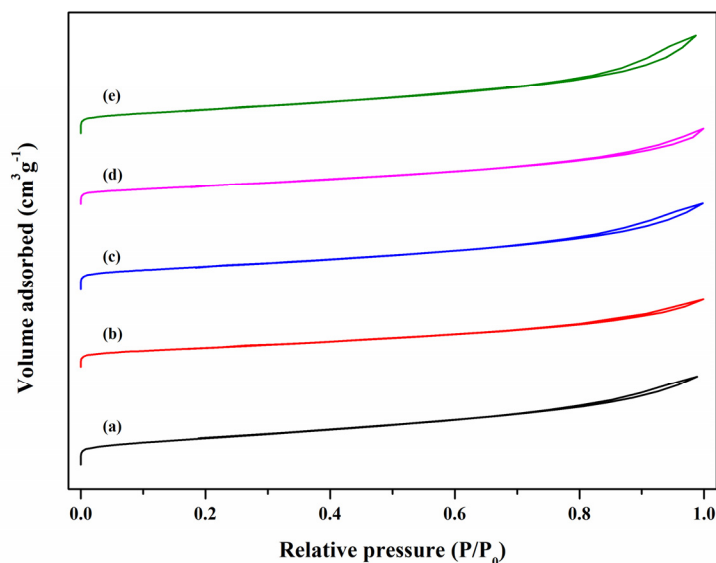


Figure 3. N_2 adsorption-desorption isotherms of (a) OMS-2, (b) 1Ni/OMS-2, (c) 3Ni/OMS-2, (d) 5Ni/OMS-2, and (e) 10Ni/OMS-2.

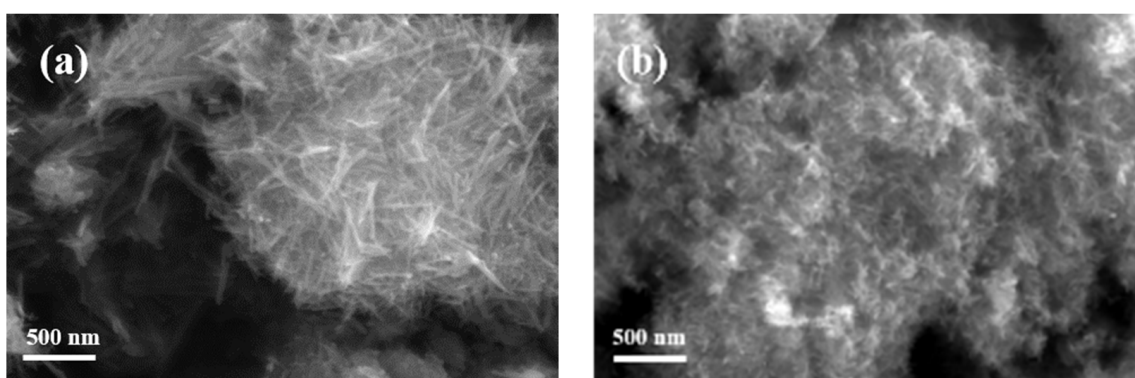


Figure 4. SEM images of (a) OMS-2 and (b) 5Ni/OMS-2.

Compared with a weight loss of 1.56 wt% at 40–250 °C of the OMS-2 support attributable to the removal of the adsorbed water, the 5Ni/OMS-2 sample displayed a weight loss of 2.07 wt% in the same temperature range, indicating that there was a greater amount of adsorbed water in 5Ni/OMS-2. The enhancement of water adsorption might be due to the loading of Ni, which made OMS-2 generate more adsorption sites. The weight loss of 5Ni/OMS-2 due to the removal of oxygen species in the second stage (250–550 °C) reached a maximal value (2.21 wt%) that was much higher than that (1.09 wt%) of OMS-2. This result might result from the generation of a greater amount of surface defects on 5Ni/OMS-2 that could provide a more amount of sites for the adsorption of oxygen molecules. Similar results were also obtained in the following XPS and O_2 -TPD characterization. According

to the literature, the strength of the $\text{Mn}^{3+}\text{-O}$ bond was weaker than that of the $\text{Mn}^{4+}\text{-O}$ bond. After Ni loading, the thermal stability of most of the samples decreased, suggesting that the loading of Ni influenced the average valence state of Mn. The decrease in thermal stability indicates that there were more Mn^{3+} ions in the $x\text{Ni}/\text{OMS-2}$ samples, which was consistent with the following Mn 2p analysis. As shown in Table 1, compared with the oxygen losses (1.09 and 3.27 wt%) of OMS-2 at 250–550 and 700–850 °C, those (2.21 and 2.55 wt%) of 5Ni/OMS-2 first increased and then decreased, respectively, which represented the enhanced mobility of lattice oxygen from bulk to surface, thus enhancing the catalytic activity of the 5Ni/OMS-2 sample.

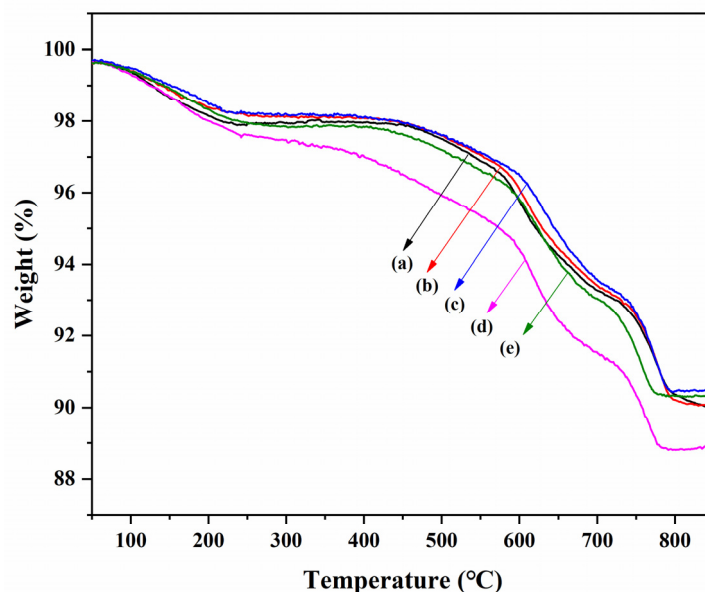


Figure 5. TGA curves of (a) OMS-2, (b) 1Ni/OMS-2, (c) 3Ni/OMS-2, (d) 5Ni/OMS-2, and (e) 10Ni/OMS-2.

Table 1. Thermal analysis of the OMS-2 and $x\text{Ni}/\text{OMS-2}$ samples.

Sample	Thermal Analysis (wt% Weight Loss)			
	40–250 (°C)	250–550 (°C)	550–700 (°C)	700–850 (°C)
OMS-2	1.56	1.09	3.69	3.27
1Ni/OMS-2	1.41	1.03	3.75	3.35
3Ni/OMS-2	1.36	1.05	3.55	3.02
5Ni/OMS-2	2.07	2.21	3.73	2.55
10Ni/OMS-2	1.66	1.47	3.58	2.63

3.6. XPS Analysis

Mn 2p, O 1s, and Ni 2p XPS spectra of the samples are shown in Figure 6, and their analysis results are listed in Table 2. As shown in Figure 6A, each Mn 2p XPS spectrum could be decomposed into three components, corresponding to the surface Mn^{4+} (binding energy (BE) = 643.5 eV), Mn^{3+} (BE = 642.2 eV), and Mn^{2+} (BE = 640.9 eV) species, respectively [20]. According to the data in Table 2, we can realize that the order of $\text{Mn}^{3+}/\text{Mn}^{4+}$ atomic ratio was 5Ni/OMS-2 (1.88) > 10Ni/OMS-2 (1.79) > 3Ni/OMS-2 (1.60) > 1Ni/OMS-2 (1.38) > OMS-2 (1.35). The surface $\text{Mn}^{3+}/\text{Mn}^{4+}$ atomic ratios on the $x\text{Ni}/\text{OMS-2}$ samples were higher than that of the OMS-2 support, with the 5Ni/OMS-2 sample possessing the highest $\text{Mn}^{3+}/\text{Mn}^{4+}$ atomic ratio. This result indicates that Ni loading could change Mn valence state distribution of the sample and an increased amount of the surface Mn^{3+} species, which was consistent with the TG analysis results.

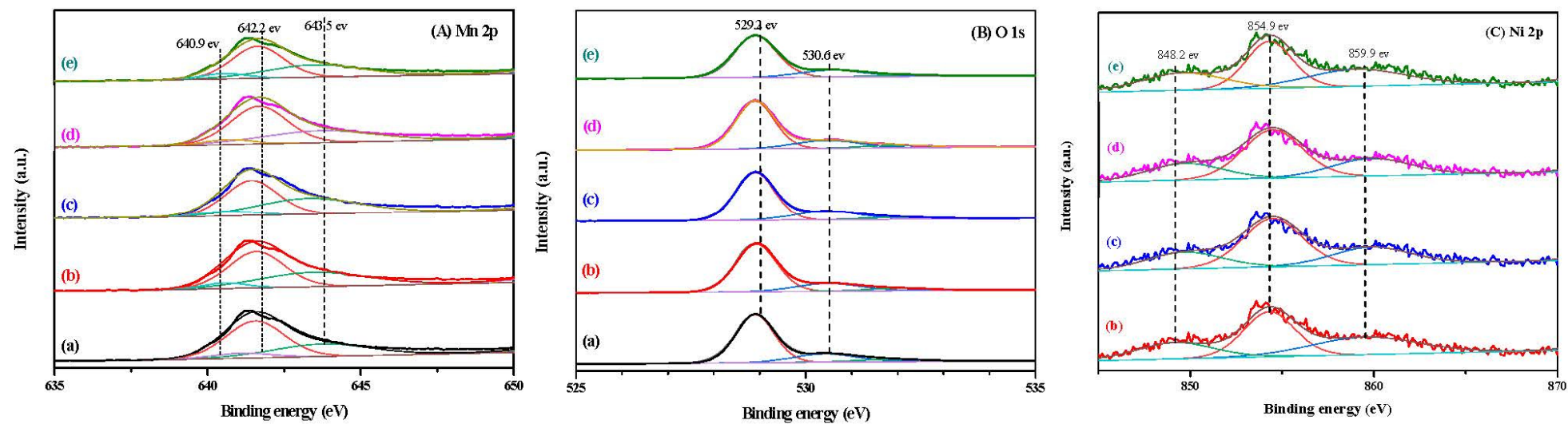


Figure 6. (A) Mn 2p, (B) O 1s, and (C) Ni 2p XPS spectra of (a) OMS-2, (b) 1Ni/OMS-2, (c) 3Ni/OMS-2, (d) 5Ni/OMS-2, and (e) 10Ni/OMS-2.

Table 2. Surface element compositions of the as-prepared samples.

Sample	Atomic Ratio		
	Mn ³⁺ /Mn ⁴⁺	O _{ads} /O _{latt}	Ni ²⁺ /Ni ⁰
OMS-2	1.35	0.25	–
1Ni/OMS-2	1.38	0.26	2.65
3Ni/OMS-2	1.60	0.28	2.86
5Ni/OMS-2	1.88	0.31	2.95
10Ni/OMS-2	1.79	0.29	3.34

O 1s XPS spectra of the samples are illustrated in Figure 6B. The two peaks at BE = 529.2 and 530.6 eV represent the surface lattice oxygen (O_{latt}) and adsorbed oxygen (O_{ads}) species, respectively [21]. As shown in Table 2, the O_{ads}/O_{latt} atomic ratio decreased in the sequence of 5Ni/OMS-2 (0.31) > 10Ni/OMS-2 (0.29) > 3Ni/OMS-2 (0.28) > 1Ni/OMS-2 (0.26) > OMS-2 (0.25). Apparently, the introduction of Ni could increase the O_{ads} concentration. This might be due to the imbalance of surface charges on the Ni-doped sample, which led to the appearance of oxygen vacancies and more surface adsorbed oxygen species, which was consistent with the TG results. It is worth noting that the 5Ni/OMS-2 sample possessed the highest O_{ads}/O_{latt} atomic ratio, coinciding with its highest Mn³⁺/Mn⁴⁺ atomic ratio. Therefore, the 5Ni/OMS-2 sample with a greater amount of oxygen vacancies possessed a greater amount of surface-adsorbed oxygen species.

As for the Ni 2p spectra of the samples, the components at BE = 854.9 and 859.9 eV belonged to the surface Ni²⁺ species, whereas the one at BE = 848.2 eV was assigned to the surface Ni⁰ species [22]. The loaded nickel was mainly present in the state of Ni²⁺ since a high Ni²⁺/Ni⁰ atomic ratio of 2.65–3.34 on the surface of the samples was obtained.

3.7. O₂-TPD Analysis

Shown in Figure 7 are O₂-TPD profiles of the OMS-2 and xNi/OMS-2 samples. There were two obvious oxygen desorption peaks, namely the low-temperature (LT) peak below 750 °C and the high-temperature (HT) peak above 800 °C. For the OMS-2 sample, the LT peak corresponded to desorption of the adsorbed oxygen as well as surface or subsurface lattice oxygen species, while the HT peak was due to desorption of the bulk lattice oxygen [23]. After loading Ni, the LT and HT peaks of all the samples shifted to a lower temperature. Ni loading caused areas of both LT and HT peaks to increase. The increase in the LT peak area was due to the fact that Ni loading made the lattice oxygen migrate from the inside of the sample to the surface, indicating that there were more oxygen vacancies on the surface of xNi/OMS-2 than those on the surface of OMS-2. The order of LT peak temperature related to desorption of the adsorbed oxygen as well as surface or subsurface lattice oxygen species was 5Ni/OMS-2 (625 °C) < 10Ni/OMS-2 (650 °C) < 3Ni/OMS-2 (670 °C) < 1Ni/OMS-2 (740 °C) < OMS-2 (755 °C). The lattice oxygen desorption temperature of 5Ni/OMS-2 was the lowest; i.e., the 5Ni/OMS-2 sample possessed the highest oxygen mobility. The strong interaction between Ni and OMS-2 could increase the diffusion rate of lattice oxygen on the surface of the sample. Among all of the samples, 5Ni/OMS-2 exhibited the most significant synergistic effect of Ni and OMS-2.

3.8. H₂-TPR Analysis

The reducibility of the as-synthesized samples was measured using the H₂-TPR technique, and the results are shown in Figure 8. Each sample shows a broad peak in the range of 75–525 °C, which can be divided into three peaks, marked as peaks α, β, and γ, respectively. For the OMS-2 support, peaks α, β, and γ correspond to the successive reduction process of MnO₂ → Mn₂O₃ → Mn₃O₄ → MnO [24]. For the xNi/OMS-2 samples, peaks α, β and γ were due to the reduction of the Mn–Ni composite oxides to MnO_x and NiO_x, respectively. After Ni loading, the initial reduction peak temperature of xNi/OMS-2 was shifted to a lower temperature as compared with that of OMS-2, indicating that the loading of Ni improved the reducibility of OMS-2 [25]. The temperature of the first

reduction peak increased in the order of 5Ni/OMS-2 (263 °C) < 10Ni/OMS-2 (268 °C) < 3Ni/OMS-2 (278 °C) < 1Ni/OMS-2 (285 °C) < OMS-2 (300 °C). Among all of the samples, 5Ni/OMS-2 exhibited the best low-temperature reducibility, since the presence of Ni could improve the migration of lattice oxygen from bulk to surface.

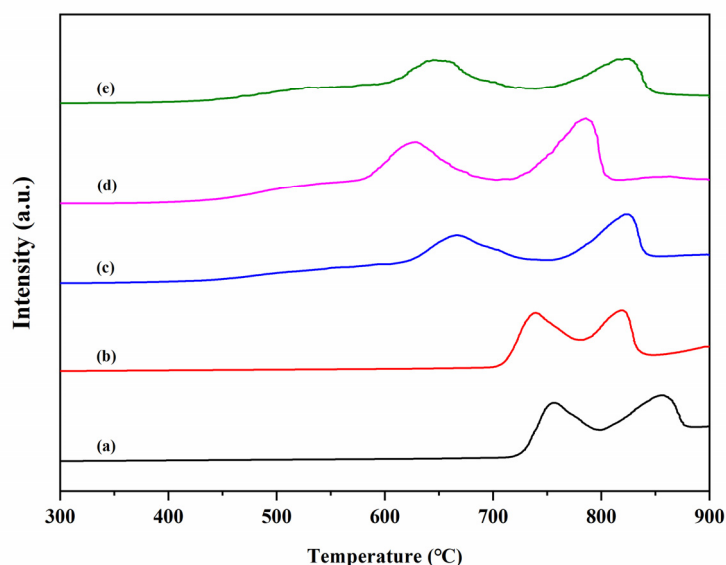


Figure 7. O₂-TPD profiles of (a) OMS-2, (b) 1Ni/OMS-2, (c) 3Ni/OMS-2, (d) 5Ni/OMS-2, and (e) 10Ni/OMS-2.

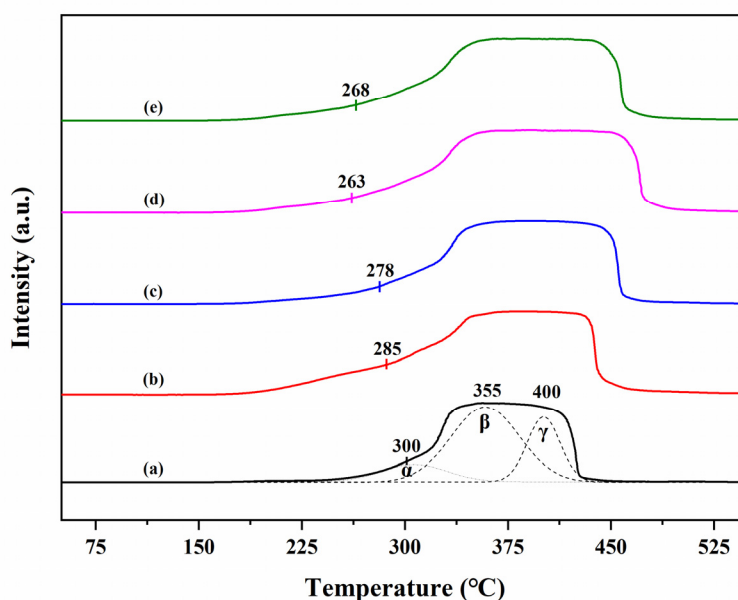


Figure 8. H₂-TPR profiles of (a) OMS-2, (b) 1Ni/OMS-2, (c) 3Ni/OMS-2, (d) 5Ni/OMS-2, and (e) 10Ni/OMS-2.

3.9. Catalytic Activity

Figure 9 depicts catalytic activities of all the samples in CO, ethyl acetate, and toluene oxidation at different temperatures, in which the SV was 60,000 mL/(g·h) for CO oxidation, whereas it was 240,000 mL/(g·h) for ethyl acetate and toluene oxidation. The reaction temperature corresponding to a conversion of x is denoted as T_x . Table 3 summarizes the T_{50} and T_{90} for CO, ethyl acetate, and toluene oxidation over all of the samples. The T_{50} and T_{90} over the OMS-2 sample were 140 and 194 °C for CO oxidation, 202 and 260 °C for

ethyl acetate oxidation, and 270 and 375 °C for toluene oxidation, respectively. After the loading of Ni, the catalytic activity of the $x\text{Ni}/\text{OMS-2}$ sample increased. In the oxidation of CO, ethyl acetate, and toluene, the $5\text{Ni}/\text{OMS-2}$ sample exhibited the highest catalytic performance, with the T_{50} and T_{90} being 115 and 155 °C for CO oxidation, 195 and 225 °C for ethyl acetate oxidation, and 240 and 300 °C for toluene oxidation, respectively.

Table 3. Catalytic activities (T_{50} and T_{90}) of the OMS-2 and $x\text{Ni}/\text{OMS-2}$ samples for the oxidation of CO at SV = 60,000 mL/(g·h), ethyl acetate at SV = 240,000 mL/(g·h), and toluene at SV = 240,000 mL/(g·h).

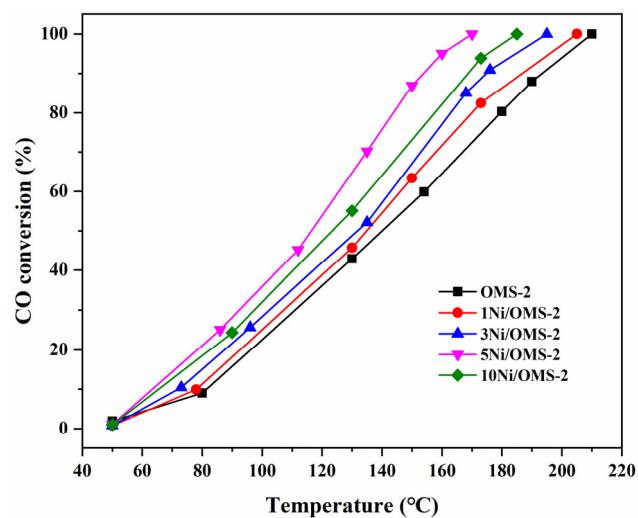
Sample	CO Oxidation	Ethyl Acetate Oxidation	Toluene Oxidation
	T_{50}/T_{90} (°C)	T_{50}/T_{90} (°C)	T_{50}/T_{90} (°C)
OMS-2	140/194	202/260	270/375
1Ni/OMS-2	135/188	200/245	255/360
3Ni/OMS-2	130/175	198/240	250/335
5Ni/OMS-2	115/155	195/225	240/300
10Ni/OMS-2	120/170	197/235	245/315

We use the specific reaction rate (r_{cat}) to compare the catalytic activity of various samples. The r_{cat} refers to the molar number of CO, ethyl acetate, and toluene converted per second per gram of catalyst ($\mu\text{mol}/(\text{g}_{\text{cat}} \cdot \text{s})$). Table 4 lists the calculated r_{cat} for CO oxidation at 145 °C, ethyl acetate oxidation at 220 °C, and toluene oxidation at 275 °C. The r_{cat} decreased in a sequence of $5\text{Ni}/\text{OMS-2} > 10\text{Ni}/\text{OMS-2} > 3\text{Ni}/\text{OMS-2} > 1\text{Ni}/\text{OMS-2} > \text{OMS-2}$. As can be clearly seen from the data in Table 4, the r_{cat} values ($3.75\text{--}5.45 \mu\text{mol}_{\text{CO}}/(\text{g}_{\text{cat}} \cdot \text{s})$) for CO oxidation at 145 °C over OMS-2 and $x\text{Ni}/\text{OMS-2}$ were much higher than that ($1.64 \mu\text{mol}_{\text{CO}}/(\text{g}_{\text{cat}} \cdot \text{s})$) over Ni/MnO₂ and that ($0.0852 \mu\text{mol}_{\text{CO}}/(\text{g}_{\text{cat}} \cdot \text{s})$) over Pd/NiMnO_x/Cord [26,27]. For ethyl acetate oxidation at 220 °C, the samples reported in the present work exhibited r_{cat} values of $2.34\text{--}4.58 \mu\text{mol}_{\text{ethyl acetate}}/(\text{g}_{\text{cat}} \cdot \text{s})$, significantly higher than that ($0.341 \mu\text{mol}_{\text{ethyl acetate}}/(\text{g}_{\text{cat}} \cdot \text{s})$) over 1Ru-5Cu/TiO₂ and that ($0.324 \mu\text{mol}_{\text{ethyl acetate}}/(\text{g}_{\text{cat}} \cdot \text{s})$) over Cu-Ce-Zr/TiO₂ [28,29]. For toluene combustion at 275 °C, OMS-2 and $x\text{Ni}/\text{OMS-2}$ showed the r_{cat} values of $2.73\text{--}3.60 \mu\text{mol}_{\text{toluene}}/(\text{g}_{\text{cat}} \cdot \text{s})$, considerably higher than that ($0.243 \mu\text{mol}_{\text{toluene}}/(\text{g}_{\text{cat}} \cdot \text{s})$) over Cu-Ce-Zr/TiO₂ and that ($0.227 \mu\text{mol}_{\text{toluene}}/(\text{g}_{\text{cat}} \cdot \text{s})$) over Ni/ α -MnO₂ [9,29]. Therefore, our samples outperformed most of the catalysts reported in the literature.

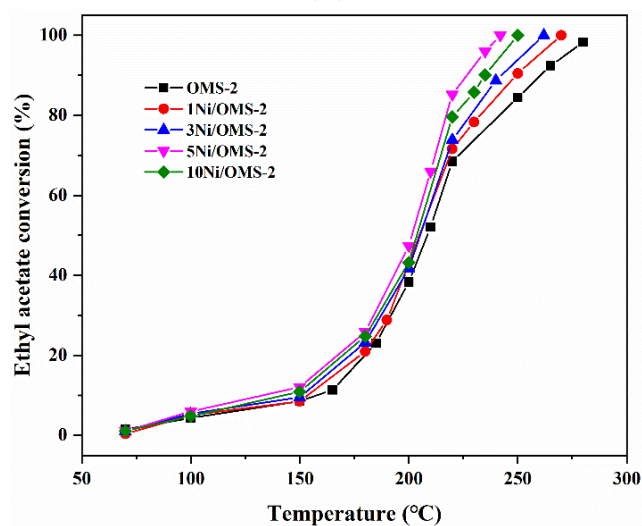
We tested the catalytic stability of the $5\text{Ni}/\text{OMS-2}$ sample for the oxidation of CO at 125 °C (T_{60}) and SV = 60,000 mL/(g·h), ethyl acetate at 210 °C (T_{70}) and SV = 240,000 mL/(g·h), and toluene at 280 °C (T_{80}) and SV = 240,000 mL/(g·h), and their results are shown in Figure 10. Obviously, there was no significant loss in catalytic activity within 50 h of on-stream reaction. The hydrophobicity of the OMS-2 surface (as revealed in the TG investigation) might be responsible for better stability, since such a unique property was favorable for decreasing the adsorption of water generated during organic oxidation at the active sites.

Table 4. A comparison on specific reaction rates for CO at 145 °C, ethyl acetate at 220 °C, and toluene at 275 °C over the catalysts reported in the present work and the literature.

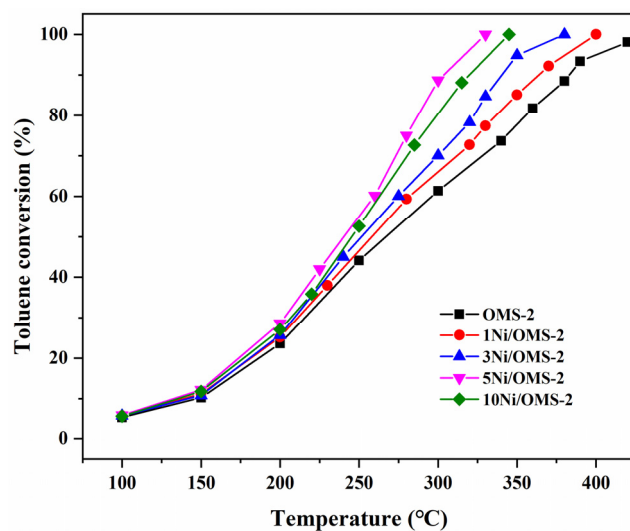
Catalyst	r_{cat} ($\mu\text{mol}_{\text{CO}}/(\text{g}_{\text{cat}} \cdot \text{s})$)	r_{cat} ($\mu\text{mol}_{\text{ethyl acetate}}/(\text{g}_{\text{cat}} \cdot \text{s})$)	r_{cat} ($\mu\text{mol}_{\text{toluene}}/(\text{g}_{\text{cat}} \cdot \text{s})$)	Reference
OMS-2	3.75	2.34	2.73	This study
1Ni/OMS-2	3.95	3.82	3.22	This study
3Ni/OMS-2	4.23	3.98	3.33	This study
5Ni/OMS-2	5.45	4.58	3.60	This study
10Ni/OMS-2	4.57	4.36	3.49	This study
Ni/MnO ₂	1.64	—	—	[26]
Pd/NiMnO _x /Cord	0.0852	—	—	[27]
1Ru-5Cu/TiO ₂	—	0.341	—	[28]
Cu-Ce-Zr/TiO ₂	—	0.324	0.243	[29]
Ni/ α -MnO ₂	—	—	0.227	[9]



(A)



(B)



(C)

Figure 9. Catalytic activity of the OMS-2 and x Ni/OMS-2 samples for the oxidation of (A) CO at SV = 60,000 mL/(g·h), (B) ethyl acetate at SV = 240,000 mL/(g·h), and (C) toluene at SV = 240,000 mL/(g·h).

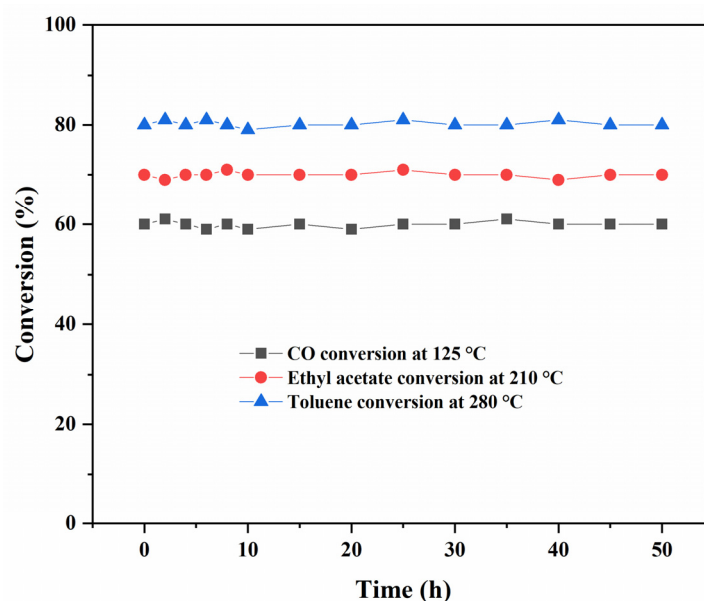


Figure 10. Catalytic stability of the 5Ni/OMS-2 sample in CO oxidation at 125 °C and SV = 60,000 mL/(g·h), ethyl acetate oxidation at 210 °C and SV = 240,000 mL/(g·h), and toluene oxidation at 280 °C and SV = 240,000 mL/(g·h).

3.10. Possible Reaction Mechanism

CO, ethyl acetate, and toluene oxidation experiments were carried out to explore their reaction mechanism over the 5Ni/OMS-2 sample. The experiment was maintained for 1 h at each temperature.

Figure 11 shows in situ DRIFTS spectra of CO oxidation over 5Ni/OMS-2 at different temperatures. There were the characteristic bands of CO at 2110–2170 cm^{-1} and bands at 1300–1600 cm^{-1} of various carbonate vibrations. When the reaction temperature rose from 70 to 170 °C, the characteristic bands of CO at 2110–2170 cm^{-1} remained unchanged, indicating that the 5Ni/OMS-2 sample showed a stable ability to adsorb CO. The absorbance of various carbonate vibrations in the range of 1300–1600 cm^{-1} was higher at 120 °C than that at 70 °C, indicating that the conversion of CO to carbonate was accelerated [30]. At 170 °C, the absorption band of carbonate species almost disappeared, indicating that the carbonate species was further decomposed at this temperature and finally converted to CO_2 . Therefore, the possible mechanism of CO oxidation on 5Ni/OMS-2 might be as follows: first, CO was adsorbed on the sample surface, then oxidized by the active oxygen species to the carbonates, and finally, the carbonates were converted to CO_2 . The consumed oxygen species were replenished by the gas-phase O_2 in the airflow to realize the catalytic cycle, as revealed in Scheme 1.

Figure 12 shows the in situ DRIFTS spectra of ethyl acetate oxidation over the 5Ni/OMS-2 sample. The absorption band of aldehyde appeared at 1775 cm^{-1} . The broad multiple bands at 1500–1700 cm^{-1} were assigned to the overlapping COO^- antisymmetric stretching vibrations of acetate and formate. The bands at 1350–1450 cm^{-1} were attributable to the COO^- symmetric stretching vibrations of acetate and formate, and the stretching vibration absorption band of CH_3 appeared at 1240 cm^{-1} [31]. As revealed in the ethyl acetate oxidation at 200 °C, the appearance of absorption bands attributable to acetate and formate at 1500–1700 and 1350–1450 cm^{-1} indicates that ethyl acetate had begun to decompose on the surface of 5Ni/OMS-2. When the temperature reached 225 °C, the intensity of the bands assignable to the acetates and formates decreased significantly, indicating that the decomposition of acetate and formate increased rapidly. When the temperature was 250 °C, there was a near absence of the intermediate products (acetate and formate), demonstrating that ethyl acetate was thoroughly oxidized to CO_2 and H_2O at this temperature. The possible mechanism of ethyl acetate oxidation over 5Ni/OMS-2

might be as follows: ethyl acetate was first adsorbed on the surface of the sample, then oxidized to acetate and formate by the reactive oxygen species, and finally rapidly oxidized to CO_2 and H_2O , as shown in Scheme 1.

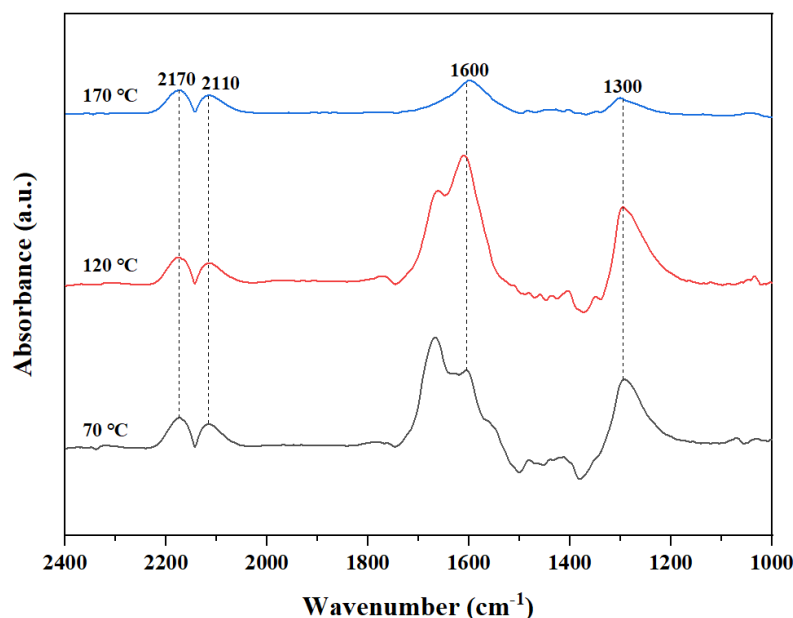
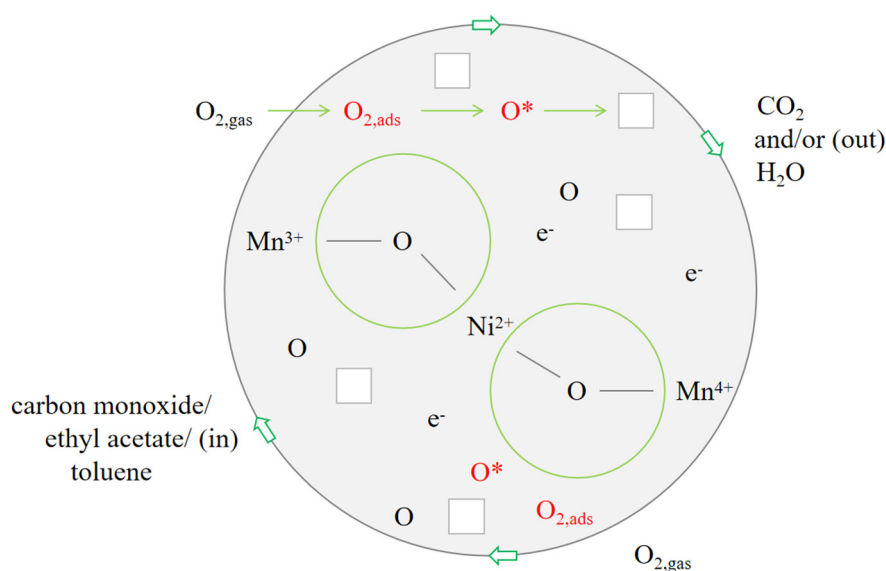


Figure 11. In situ DRIFTS spectra of the 5Ni/OMS-2 sample in a 1.08 vol% CO/air (balance) feed gas at different temperatures.



Scheme 1. Possible reaction mechanisms of CO, ethyl acetate, and toluene oxidation over the 5Ni/OMS-2 sample.

Figure 13 shows in situ DRIFTS spectra of toluene oxidation over the 5Ni/OMS-2 sample at different temperatures. The absorption bands at $1600\text{--}1800\text{ cm}^{-1}$ were assigned to the stretching vibration of $\text{C}=\text{O}$, which indicates that there were intermediate products during the reaction process [32]. The bands at $1450\text{--}1550\text{ cm}^{-1}$ were attributed to the carboxylic acid group. Meanwhile, a higher intensity of the band ascribable to the carboxylate species at $1450\text{--}1550\text{ cm}^{-1}$ suggests that benzoate was likely to be a key intermediate involved in toluene oxidation. The band at 2355 or 2335 cm^{-1} was related to the gaseous or adsorbed CO_2 [33]. As revealed in toluene oxidation at $150\text{ }^\circ\text{C}$, toluene was decom-

posed on the surface of 5Ni/OMS-2 due to the appearance of the bands at 1600–1800 and 1450–1550 cm^{-1} (belonging to C=O and benzoate). As the temperature increased to 250 °C, the bands 1450–1550 cm^{-1} due to benzoate were recorded, but they disappeared at 350 °C, where toluene was completely converted into H_2O and CO_2 . Therefore, a possible catalytic oxidation mechanism was proposed as follows: toluene was first adsorbed at the active center of 5Ni/OMS-2; before toluene was completely converted to carbon dioxide and water, it was first transformed to benzoate and then to carbonate, which left the surface of 5Ni/OMS-2 to form oxygen vacancies; subsequently, 5Ni/OMS-2 picked up oxygen in the airflow to supplement the oxygen vacancies, as illustrated in Scheme 1. The results show that lattice oxygen, especially reversibly exchanged active lattice oxygen, might play a decisive role in enhancing catalytic performance of 5Ni/OMS-2.

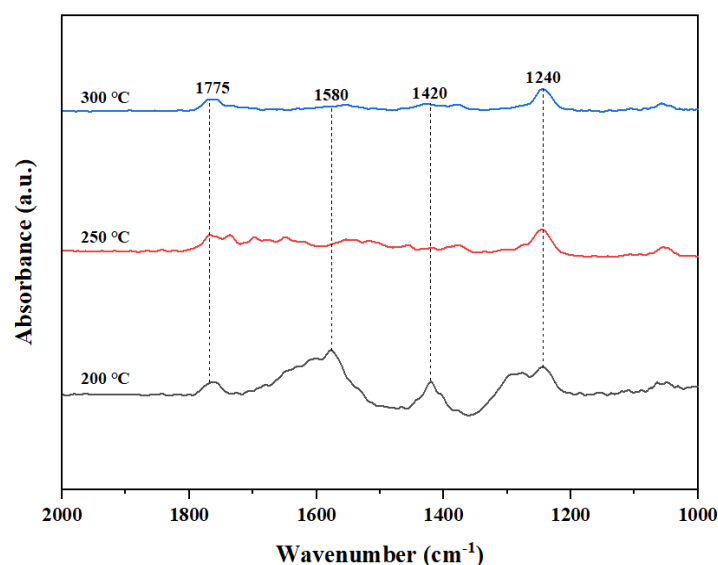


Figure 12. In situ DRIFTS spectra of the 5Ni/OMS-2 sample in a 2000 ppm ethyl acetate/ O_2/N_2 feed gas at different temperatures.

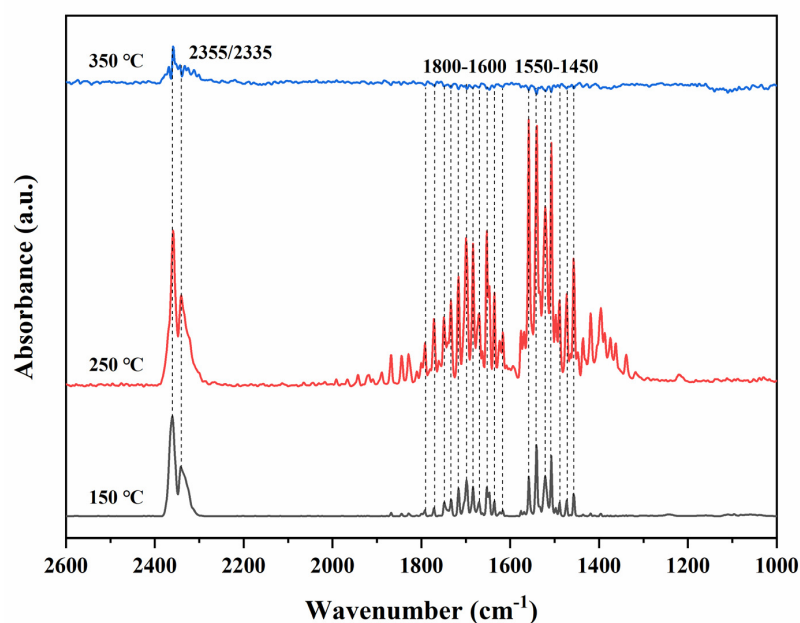


Figure 13. In situ DRIFTS spectra of the 5Ni/OMS-2 sample in a 2000 ppm toluene/ O_2/N_2 feed gas at different temperatures.

After loading the transition metal Ni, the redox property of the OMS-2 sample changed greatly, especially that of the 5Ni/OMS-2 sample. Specifically, 5Ni/OMS-2 had the lowest reduction temperature (263 °C). Compared with those on the other samples, the O_{ads}/O_{latt} ratio on the 5Ni/OMS-2 sample was the highest. The doping of Ni could enhance the strong metal–support interaction, generating the $xNi/OMS-2$ samples with good catalytic performance, which could be used for the oxidation of CO, ethyl acetate, and toluene.

4. Conclusions

The $xNi/OMS-2$ samples were prepared using the pre-incorporation method, and their catalytic activities for CO, ethyl acetate, and toluene oxidation were evaluated. A series of characterization results demonstrate that the loaded Ni amount exerted a considerable influence on the physicochemical property of the sample. The 5Ni/OMS-2 sample showed the best catalytic activity: T_{90} was 155 °C for CO oxidation at SV = 60,000 mL/(g·h), 225 °C for ethyl acetate oxidation at SV = 240,000 mL/(g·h), and 300 °C for toluene oxidation at SV = 240,000 mL/(g·h). The good catalytic activity of 5Ni/OMS-2 was associated with its rich exchangeable lattice oxygen, high Mn^{3+} content and lattice oxygen mobility, good low-temperature reducibility, and strong interaction between nickel and manganese oxide. The possible pathways of carbon monoxide, ethyl acetate, and toluene oxidation were as follows: (i) for CO oxidation, $CO + O_2 \rightarrow$ carbonate species $\rightarrow CO_2$; (ii) for ethyl acetate oxidation, ethyl acetate + $O_2 \rightarrow$ acetate and formate species $\rightarrow CO_2 + H_2O$; and (iii) for toluene oxidation, toluene + $O_2 \rightarrow$ benzoate and carbonate species $\rightarrow CO_2 + H_2O$.

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Conflicts of Interest: The authors declare no conflict of interest.

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