



Research on the complete oxidation of volatile aromatic compounds based on cobalt oxide based catalysts

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ABSTRACT

VOCs are a group of compounds that have negative impacts on the environment and humans. VOCs can be treated by many methods, notably the catalytic oxidation method. In this study, the synthetic catalysts were MnCoCe oxide and NiCo oxide supported on cordierite. The typical analytical methods used include SEM EDX, XRD, N₂ adsorption-desorption isotherms, TPD-O₂, and TPR-H₂. GC and GC-MS were used to analyze the gas composition. The catalyst has high activity at temperatures above 300 °C. MnCoCe oxide/cordierite completely converts toluene with 100% selectivity to CO₂ at 350 °C. NiCo oxide/cordierite has lower activity, converting 80% toluene with 100% CO₂ selectivity.

Introduction

Emissions containing Volatile organic compounds (VOCs) are one of the causes that seriously affect the air environment and human health [1]. Based on the boiling temperature of the components, VOCs are defined quite clearly technically: "VOCs mean any compounds of carbon with volatility feature, which have an initial boiling point less than or equal to 250°C measured at a standard atmospheric pressure of 101.3 kPa" [2].

VOCs in the atmosphere are of natural or anthropogenic origin [3]. Some biological VOCs, such as terpenes, linalyl acetate, and linalool, benefit human life [4,5] but VOCs usually have negative impacts include stratospheric ozone depletion, climate change, and photochemical smog [1,3]. Large amounts of VOCs (aromatic hydrocarbons, aldehydes, ketones, and alcohols) are highly toxic and carcinogenic [3].

Anthropogenic sources emit more than 1.42×10^8 tons of carbon per year as VOCs [6]. Rice straw open burning

(RSOB) emits 32 Mg for total 10 particle-bound polycyclic aromatic hydrocarbons (PAHs) to the atmosphere in Hanoi [7]. Toxic organic compounds (benzene, toluene, acetaldehyde, iso-pentane, etc.) were found from transportation activities in Hanoi and Ho Chi Minh [8]. The concentration of benzene in Ho Chi Minh City (HCMC) is higher than the national standard QCVN 06:2009/BTNMT by about ten times [9].

Many methods can be applied to reduce the amount of VOCs emitted into the environment, such as the biological method, thermal oxidation method, catalytic oxidation method, adsorption method, absorption method, etc [10]. Each method has its advantages and disadvantages, but the catalytic oxidation method shows many outstanding advantages such as long-lasting catalysts, reduced activation energy, and reduced emissions of toxic waste.

Noble metal catalysts are highly active but expensive and easily deactivated in the presence of chlorine. In contrast, transition metal oxides are readily available,

inexpensive, have long lifetimes, are easily regenerated, and are more resistant to allergens [1,3]. Many studies have shown that Co catalysts are capable of completely oxidizing VOCs at low temperatures due to the presence of mobile oxygen in their spinel-like structure (Co_3O_4) [11-16]. When doping other metals into Co spinel-based oxides (Co_2MO_4 , M: transition metal), it can affect the catalytic activity. The catalytic activity depends on the utilization of lattice oxygen and the coordination between metal cations, etc. [17]. MnO_x and Co_3O_4 oxide are cheap, highly active, and treat many types of VOCs [1]. CeO_2 addition increases oxygen storage capacity, resulting deep toluene oxidation at low temperatures [18,19]. The addition of Ni to Co_3O_4 forms the spinel structure NiCo_2O_4 , improves activity, and lower the reaction temperature than that of the single metal oxides [20].

Pollutants can be completely oxidized at moderate temperatures (from 200-500 °C) [21]. The experimental results were completely consistent when studying the ability to treat toluene on the synthesized NiCo oxide/cordierite and MnCoCe oxide/cordierite catalyst systems. Besides, in the reaction, the role of catalyst is very important. To improve the activity of catalyst, several properties need to be considered such as specific surface, thermal stability, the dispersion of active sites. Therefore, in this study, catalysts' properties are studied with the aim of improving the efficiency of the catalysts.

Experimental

Catalyst synthesis

The catalysts were synthesized as MnCoCe oxide and NiCo oxide on cordierite ceramics by the impregnation method. The catalysts were synthesized according to the molar ratio of $\text{MnO}_2/\text{Co}_3\text{O}_4/\text{CeO}_2=1/3/0.19$ and $\text{Ni}^{2+}/\text{Co}^{2+}=1/2$.

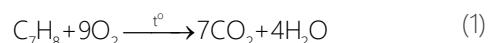
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (7.7698 g), solution $\text{Mn}(\text{NO}_3)_2$ 50% (1.0617 g), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.2447 g), cordierite (1.8466 g) were used to synthesize MnCoCe oxide/cordierite. Chemicals used to synthesize NiCo oxide/cordierite included $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (11.8182 g), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5.9086 g), and cordierite (2.0037 g).

Initially, the transition metal oxide precursors (which are metal nitrate salts) were dissolved in a beaker containing 8 mL of double distilled water. Stirring (500 rpm) with heating (50 °C) for 2 hours. Then, the cordierite ceramics were soaked for 1 hour, and the ceramic surface was dried at 110 °C for 1 hour. When the ceramic pellets were completely dry, they were pre-calcinated at 300 °C, with

a heating rate of 3 °C/min. The pre-calcination time was 1 hour. Repeat the impregnation process 5 times. The impregnation solution was dried at 120 °C and calcined under the same conditions as the cordierite ceramic sample carrying the active phase (sintering temperature 500 °C, 3 hours, heating rate 2 °C/min). After synthesis, the active phase MnCoCe oxide and NiCo oxide carried on the cordierite ceramic was 32.92% and 37.16%, respectively.

Catalytic activity test

The equation represents the complete oxidation reaction of toluene:



Catalytic activity was studied on a fixed bed catalytic reaction system. 0.1 gram of catalyst was used for the reaction. Survey temperatures range from 150 °C to 350 °C. The O_2 flow rate was 14.17 mL/min, the N_2 flow rate through the toluene bubbler was 13.39 mL/min and the total flow (including N_2 , and O_2) was 19.06 mL/min. N_2 gas stream is bubbled into the toluene tank (0 °C) and saturated with toluene vapor (7900ppm) (O_2 gas is turned on but not through the bubbler). Then, the oxidation reaction is carried out. The online gas chromatograph with a TCD detector was used to detect the gas composition. In addition a gas chromatograph with a mass spectrometry detector (GC-MS) was used to determine the gas composition before and after treatment to fully analyze the components in the bypass sample and the oxidation products. The GC-MS is the Trace 1310 - ISQ7000 using a CP-SilicaPLOT 30m x 0,32mm analytical column (4 μm thick film). The temperature program was maintained at 35 °C for 4 minutes, increased at a rate of 10 °C/minute to 190 °C, and held for 5 minutes.

Calculation of conversion and selectivity

The following formula determines toluene conversion:

$$\eta_{toluen} = \left(1 - \frac{C_{toluen}^t}{C_{toluen}^o} \right) \times 100\% \quad (2)$$

In which, η_{toluen} is the conversion of toluene (%), C_{toluen}^t is the concentration of toluene at time t (ppm), C_{toluen}^o is the saturation concentration of toluene (ppm).

The equation determines the conversion of toluene to CO_2 :

$$\gamma_{CO_2} = \frac{C_{CO_2}^t}{7 \times (C_{toluen}^o - C_{toluen}^t)} \times 100\% \quad (3)$$

In which, γ_{CO_2} is the conversion rate of toluene to CO_2 (%), $C_{CO_2}^t$ is the concentration of CO_2 formed at time t (ppm).

Catalyst characterization

The methods for studying the catalyst characterization include X-ray diffraction (XRD, D8 Advance-Brucke, CuK α wavelength is 0.15406 nm; scanning speed is 0.02°/s, scanning angle 2 θ varies from 10° to 70°), scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDX, JCM-7000 NeoScope™ Benchtop), temperature-programmed desorption TPD-O₂ and temperature-programmed reduction TPR-H₂ (Auto-Chem 2920 II - Micromeritics device), and N₂ adsorption - desorption isothermal method (Micromeritics Gemini VII 2390 device).

Results and discussion

XRD crystal diffraction analysis results

In the X-ray diffraction pattern of MnCoCe catalyst, the MnCo₂O_{4.5} crystalline phase appeared at 2 θ angles of 18.9°; 31.1°; 36.8°; 44.8°; 59.4° and 65.2°, but the crystalline phase of Ce element did not appear due to the small content in the sample [22]. With the NiCo oxide sample synthesized at the molar ratio Ni²⁺/Co²⁺ = 1/2, the characteristic peaks of NiCo₂O₄ oxide appeared at 2 θ scanning angles of 18.91°, 31.24°, 36.60°, 44.70°, 59.09°, 65.29° [23]. All peaks are well indexed to the cubic phase NiCo₂O₄ (JCPDS card no. 20-0781) and the absence of any unidentified peaks in the XRD pattern also indicates the purity of the calcined powder.

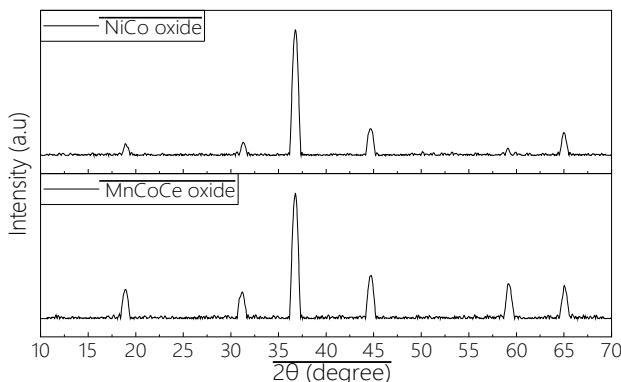


Fig. 1: X-ray diffraction patterns

N₂ adsorption-desorption isotherm results

The specific surface areas of MnCoCe oxide and NiCo oxide powder samples were determined by the N₂ adsorption-desorption isotherm method. The specific surface area of MnCoCe oxide and NiCo oxide powder samples were 25.5 m²/g and 10.7 m²/g, respectively.

SEM-EDX Mapping results

When observed by an optical microscope with 4x magnification, the surface of cordierite ceramic before

and after impregnation with active phase has obvious changes. After impregnation, the ceramic surface changes from white to black due to the presence of metal oxides. The particle size is smaller as the active phase MnCoCe oxide and NiCo oxide covering the ceramic surface. The observed image shows that NiCo oxide does not completely cover the ceramic surface. Thus, the results show that the oxides have been successfully impregnated on ceramic but the ability to carry the active phase MnCoCe oxide onto cordierite is higher than that of the NiCo oxide sample.

Scanning electron microscope image with 2000x magnification shows that the surface of the NiCo oxide/cordierite sample is covered with very small particles, uneven in size. In contrast, MnCoCe oxides are linked together into a large mass, forming gaps like capillaries.

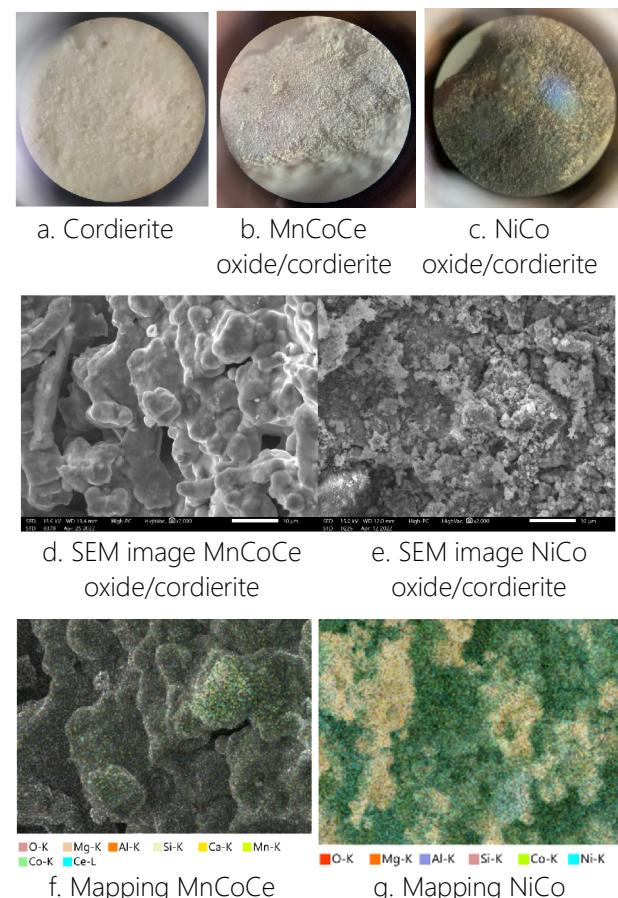


Fig. 2: SEM, mapping, and optical microscope images

The EDX analysis results showed the presence of the elements O, Mg, Al, Si, Ca, Mn, Co, and Ce in the MnCoCe oxide/cordierite sample. The atomic compositions are 17.07%, 0.57%, 1.87%, 0.48%, 0.31%, 5.01%, 72.50%, and 0.34% respectively (error no more than 1.85 %). With the NiCo oxide/cordierite sample, the

elements O, Mg, Al, Si, Co, and Ni appeared. The atomic compositions are 52.46%, 0.59%, 0.13%, 0.16%, 24.55%, and 22.15% respectively (error not more than 0.46%). These elements were not evenly distributed on the sample surface. The appearance of Mg, Al, Si, and Ca is due to the composition of cordierite ceramic [22,23].

TPR-H₂ temperature programmed reduction results

The total H₂ consumption of the MnCoCe oxide sample reached 9.73 mmol/g, nearly 5 times higher than that of the NiCo oxide sample (2.08 mmol/g). The TPR-H₂ results are shown in Fig. 3. With the NiCo oxide sample, there were two reduction peaks at temperatures of 170 – 360 °C and 360 – 500 °C. The first reduction peak occurred at low temperature, with a higher H₂ consumption than the second peak. In the temperature range of 240 – 360 °C, NiCo oxide was reduced by H₂ to NiCoO₂ (Co³⁺ was reduced to Co²⁺), reducing the catalytic activity [24]. The second peak was assigned for the reduction of the Ni-Co-O bimetallic oxide. Peres et al. found that in the temperature range of 350 – 550 °C, there was an overlap of the reduction peaks of Ni²⁺ to Ni⁰ and Co²⁺ to Co⁰ [25]. This result is completely consistent with the study of Wang et al. (2019): the reduction peak at 340 – 400 °C completely reduced the metal oxide to nickel and cobalt. Compared to pure Co₃O₄ with reduction peaks at 352 °C and 674 °C, pure NiO with a characteristic reduction peak at 338 °C, NiCo oxide has a reducing property at much lower temperatures [24].

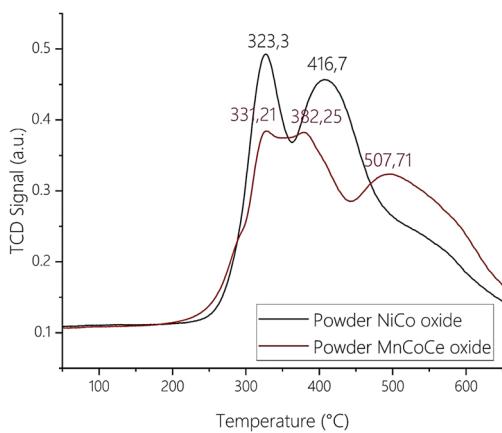


Fig. 3: TPR-H₂ profiles

With the MnCoCe oxide sample, 2 reduction peaks appeared in the temperature range of 200 – 450 °C, corresponding to the typical two reduction steps of MnO₂: the first step is ascribed to the reduction of MnO₂ to Mn₃O₄, and the second step is ascribed to the combined reduction of Mn₃O₄ to MnO and Co³⁺ to Co²⁺. M.T. Le et al. reported that MnCoCe oxide sample (molar ratios of MnO₂/Co₃O₄/CeO₂= 21/63/16) was

reduced with two reduction peaks appeared at lower temperature than pure MnO₂ (reduction peak at 425 °C) and MnO₂-Co₃O₄ mixture (reduction peak at 353 °C and 480 °C), but there was also an additional reduction peak at 507.71 °C [26], [27]. The appearance of this reduction peak is due to the strong interaction between manganese-cobalt and ceria [28].

TPD-O₂ results

The amount of O₂ desorbed changes according to the temperature of metal oxide powder samples. The total amount of desorbed oxygen (from 100 °C to 700 °C) in the NiCo oxide powder sample is 4.90 mmol/g, 19.71 times higher than that of the MnCoCe oxide powder sample (0.25 mmol/g). The MnCoCe oxide sample has 3 desorption peaks at 201.5, 570.8, and 699.3 °C. At 201.5 °C, desorption of chemically adsorbed oxygen (surface active oxygen) or physically adsorbed oxygen occurs. At temperatures higher than 500 °C, desorption of the bulk lattice oxygen (O²⁻) occurs [28]. The NiCo oxide sample has only 1 desorption peak at 699.4 °C. The initial desorption temperature of NiCo oxide is very high, possibly due to the structural oxygen of NiCo. At low temperatures (\leq 250 °C), the NiCo sample does not desorb oxygen while the MnCoCe oxide sample desorbs a large amount of oxygen (0.19 mmol/g). Thus, the MnCoCe sample has a higher oxygen adsorption capacity than the NiCo sample, so its activity is higher.

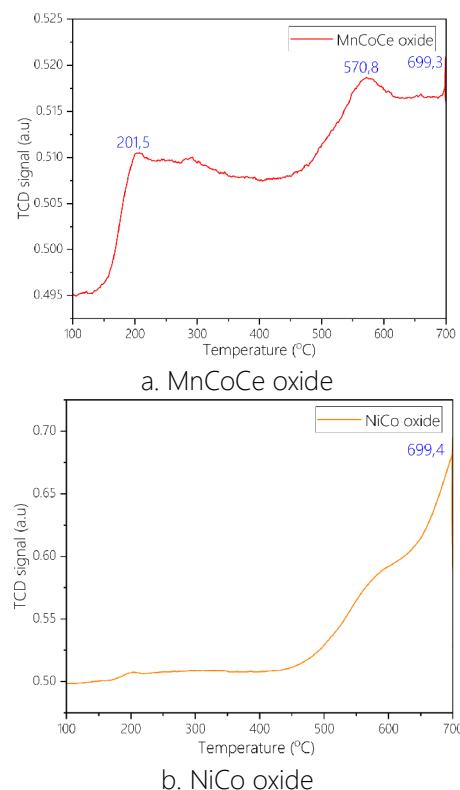


Fig. 4: TPD-O₂ profiles

Catalytic activity results

The research results show that the MnCoCe oxide powder sample has higher activity than the MnCoCe oxide/cordierite sample. On the contrary, the opposite is true for catalysts containing NiCo oxide. Adsorption force, intermediates formed, etc. are the reasons leading to abnormal changes in CO_2 conversion and selectivity in the oxide powder samples and have different effects on each catalyst system (powder sample and ceramic sample). At temperatures lower than 250 °C, the conversion and selectivity are low due to the large adsorption affinity, forming incomplete oxidation products such as acetic acid, benzyl alcohol, phenol, and CO [29]. Catalytic activity increases very rapidly in the range 250 ÷ 350 °C.

MnCoCe oxide catalyst is capable of completely converting toluene into CO_2 and H_2O without forming by-products at 300 °C (powder sample) and 350 °C (ceramic sample). MnCoCe oxide catalyst has higher activity than NiCo oxide due to its higher oxygen adsorption capacity and metal oxide reduction occurs in the reaction temperature range investigated (from 150 °C to 350 °C).

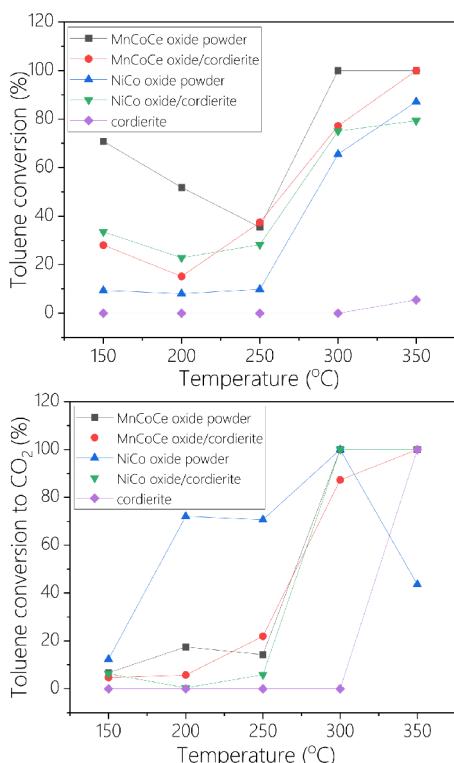


Fig. 5: Catalytic activity results

The research results show that cordierite is not effective in treating toluene at low temperature. At high temperatures (from 350 °C), toluene started to be oxidized by raw oxygen gas, forming only CO_2 and H_2O .

The efficiency for treating toluene of NiCo oxide (powder and ceramic samples) is only about 80-90% at 350 °C and less than 40% at temperatures lower than 250 °C. The catalytic activity of the NiCo oxide/cordierite catalyst was higher than that of the NiCo oxide powder sample but still lower than that of the MnCoCe oxide catalyst.

GC-MS analysis results

GC-MS analysis showed that toluene was 100% converted to CO_2 and H_2O when using MnCoCe oxide powder catalyst. The oxidation products and unreacted reactants at temperature 300 °C and 350 °C when using MnCoCe oxide/cordierite, NiCo oxide/cordierite, NiCo oxide powder are N_2 , O_2 , CO_2 , H_2O and toluene as appeared in GC-MS spectra. Although MnCoCe oxide/cordierite completely oxidized toluene at 350 °C, GC-MS analysis still detected trace amounts of toluene. The chromatograms and mass spectra obtained when analyzing the oxidation products of NiCo oxide catalyst samples (powder and ceramic sample), MnCoCe oxide (ceramic sample) are shown in Fig. 6.

Conclusion

In this study, MnCoCe and NiCo catalysts were successfully synthesized and carried on the surface of cordierite ceramics with active phase contents of 32.92% and 37.16% by mass, respectively. The catalyst samples were completely treated toluene at temperatures above 250 °C. The process of carrying the active catalytic phases on the surface of cordierite ceramics did not change the properties of the catalysts and maintained the catalytic activity with a lower active phase content than that of the powder sample. The characterization methods showed that the good oxidizing ability of the MnCoCe catalyst may be due to the mobility of surface oxygen at low temperatures.

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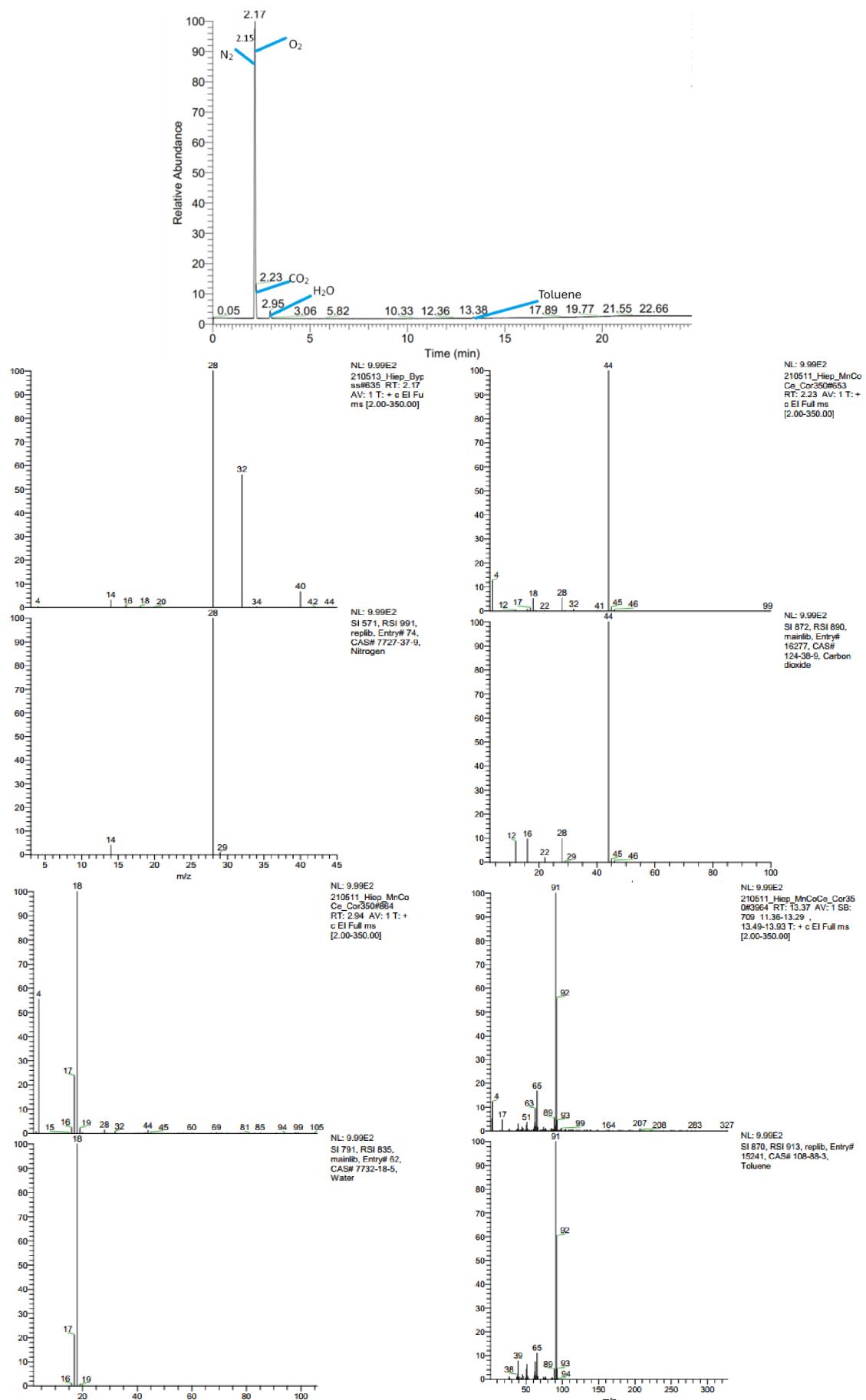


Fig. 6: GC-MS analysis of toluene oxidation products on MnCoCe oxide/cordierite at 350 °C

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