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Toluene oxidation catalyzed by NiO/SiO_2 and $NiO/TiO_2/SiO_2$: Towards development of humidity-resistant catalysts

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ABSTRACT

Toluene oxidation was catalyzed by NiO/SiO_2 and $NiO/TiO_2/SiO_2$ under dry and highly humid (relative humidity = 70%) conditions at 250 and 350 °C. At 350 °C, both catalysts showed nearly complete removal of toluene and conversion of toluene to CO_2 under humid as well as dry conditions. Catalytic activity of the NiO/SiO_2 was significantly decreased by the increase in the humidity at 250 °C, whereas that of $NiO/TiO_2/SiO_2$ was much less sensitive to the humidity. A facile adsorption of water on NiO/SiO_2 due to the hydrophilic nature of SiO_2 surface resulted in a pronounced suppression of toluene adsorption on the surface and lower catalytic activity under humid conditions. On the contrary, a higher affinity of TiO_2 towards toluene adsorption even under highly humid conditions can allow more humidity-independent catalytic activity of $NiO/TiO_2/SiO_2$. We suggest that the modulation of surface structure of supporting materials of nanoparticle catalysts can be useful for fabrication of more humidity-resistant heterogeneous catalysts.

1. Introduction

Various volatile hydrocarbon molecules can be emitted from the automobile exhausts and catalytic oxidation of these emitted hydrocarbon molecules into CO_2 and H_2O is an important issue in environmental science and technology [1–6]. Also, volatile organic compounds (VOCs) existing in the indoor environments can be harmful to the human kinds, and thus, removal of VOCs by catalytic oxidation has been drawing much attention [2,4,5]. Among various VOCs, toluene has been regarded as one of the most harmful and abundant pollutants [7–10].

Generally, noble metals such as Pt and Pd have been found to show very high activity and selectivity towards catalytic total oxidation of VOCs [11–15]; however, these are known to be expensive and therefore, more economic alternatives have been searched for the last several decades [16–20]. It has been found that less expensive materials such as Mn-oxide, Cu-oxide and Ni-oxide can also show substantially high activity towards oxidation of VOCs [16,20–25]. There are some materials, which are generally known to be catalytically less reactive; however, there can be a drastic increase in the catalytic activity as the materials exist in the form of very thin film or nanoparticles less than 5 nm in diameter [11,13,15]. Primarily, increase in the specific surface areas of catalytic particles by decreasing particle size or thickness can result in a higher catalytic activity, and in addition, increase in the number of active sites such as corners and particle/support interfaces can also result in enhanced catalytic activity. Recently, supported NiO nanoparticles or thin films were suggested to be reactive for oxidative catalytic reactions, and much attention has been paid to the NiO-based catalysis [26–28].

Catalytic activity can be much influenced by the humidity of the atmosphere; a lower humidity can act positively to the catalytic activity since OH groups formed by dissociative chemisorption of water vapor can efficiently oxidize hydrocarbon [29–34]. However, a higher humidity can have a negative effect, since water molecules adsorbed on the surface of catalyst can block adsorption of other reactant molecules, lowering catalytic conversion efficiency [24,35–39]. Development of heterogeneous catalysts operating with a constant reactivity under variously humid conditions is highly required.

In the present work, we show toluene oxidation catalyzed by two different NiO-based catalysts, which are NiO nanoparticles supported by bare and TiO_2-coated mesoporous SiO_2, respectively. We used different humidity and temperature conditions for the toluene oxidation experiments. Reaction temperatures

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of 250 °C and 350 °C were chosen: 350 °C is a temperature, which ensures complete total oxidation of toluene using catalysts, whereas at 250 °C, non-complete total oxidation and significant change in the toluene oxidation activity as a function of reaction time can be observed. These are also in the range of typical working temperatures of NiO-based catalyst for toluene oxidation [25]. Moreover, strategies for developing humidity-insensitive catalysts by modulating substrate surface structure will be discussed.

2. Experimental

2.1. Sample preparation

NiO/SiO_2 and $NiO/TiO_2/SiO_2$ catalysts were prepared by atomic layer deposition (ALD) method, and Table 1 shows the detailed parameter of ALD process used in this study. Prior to the ALD process, the mesoporous SiO_2 (average pore size = 13.8 nm, Aldrich) was outgassed at 500 °C for 3 h under ambient pressure conditions. For the deposition of NiO, 0.6 g of outgassed mesoporous SiO_2 was placed in an ALD reactor and exposed to bis(cyclopentadienyl) nickel ($Ni(Cp)_2$, Aldrich) vapor with a working pressure of 200 mtorr and O_2 with 1.3 torr for 30 and 40 s, respectively, in an alternate manner. During the ALD process, the sample temperature was maintained at 260 °C, whereas those of $Ni(Cp)_2$ and O_2 bottles at 60 °C and room temperature, respectively.

$NiO/TiO_2/SiO_2$ catalyst was prepared by depositing TiO_2 first and subsequently NiO on the outgassed mesoporous SiO_2 using ALD. For TiO_2 deposition, titaniumtetraisopropoxide ($[Ti(OCH(CH_3)_2)_4]$, TTIP, Aldrich) and H_2O were used as precursors of Ti and O, respectively. The sample temperature was kept at 150 °C, whereas TTIP and H_2O bottles at 50 °C and room temperature, respectively, during ALD of TiO_2. TTIP precursor with a working pressure of 400 mtorr was exposed to the sample for 40 s and subsequently H_2O with 400 mtorr for 50 s. After the TiO_2 deposition, the sample was transferred to another ALD reactor for NiO deposition using the same method as that for the preparation of NiO/SiO_2. In all the ALD processes, the base pressure was maintained below 10 mtorr and high purity N_2 (99.999%) gas was used as purging gas between the precursor exposing steps. 40 and 50 cycles of ALD were used for the deposition of NiO and TiO_2, respectively.

2.2. Sample characterization

The elemental compositions of NiO/SiO_2 and $NiO/TiO_2/SiO_2$ catalyst were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, 720-ES, Agilent) and the surfaces of the catalysts were analyzed using x-ray photoelectron spectroscopy (XPS) equipped with concentric hemispherical analyzer (CHA, PHOIBOC-Has 2500, SPECS) and monochromatic X-ray source (Mg Kα, 1253.6 eV). The morphological images of samples were obtained using scanning transmission electron microscopy (STEM, JEM-3010, JEOL). The N_2 adsorption-isotherm was used to evaluate the surface area and pore size distribution of samples based on the BET (Brunauer-Emmett-Teller) and BJH (Barett-Joyer-Halenda) analyses, respectively. All of the analyses were carried out on the samples outgassed at 500 °C for 90 min under a constant flow of air.

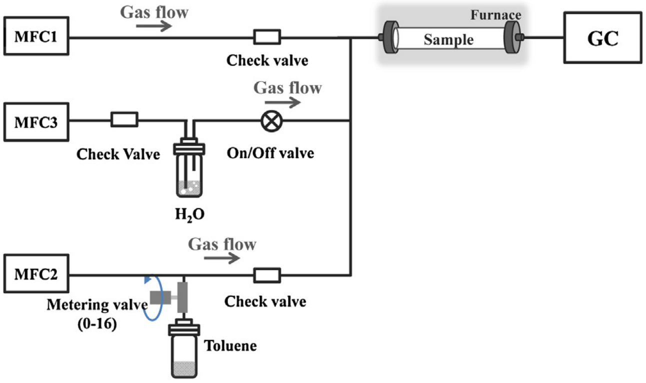

Figure 1. Experimental set-up for the toluene oxidation experiments under dry and humid conditions at various temperatures is schematically illustrated.

2.3. Catalytic activity measurements

Catalytic activities of NiO/SiO_2 and $NiO/TiO_2/SiO_2$ for toluene combustion were evaluated under dry and humid conditions. Figure 1 shows a schematic diagram of experimental set-up for toluene combustion with a humidity control system. The set-up consisted of the gas preparation stage, the reactor with furnace and gas chromatograph (GC, Agilent-6890 N) equipped with methanizer and flame ionization detector (FID). The gas preparation stage was composed of three mass flow controllers (MFCs) and two bottles filled with toluene (Aldrich, purity 99.8%) and distilled water, respectively. Temperatures of toluene and distilled water bottles were maintained at 30 °C, and MFC 1, 2 and 3 provided constant flows of dry air, humid air and dry air mixed with toluene to the reactor, respectively. 0.5 g of a catalyst was packed in the quartz reactor using quartz wool and outgassed at 500 °C for 90 min under a flow of 20 sccm of dry air to remove impurities of the catalyst. Then, the temperature of the reactor was cooled down to either 250 °C or 350 °C for toluene combustion experiments. After the temperature of the reactor was stabilized, either dry or humid airs containing toluene vapor with a concentration of ~ 80 ppm was introduced into the reactor with a total flow of 20 sccm and the flow was maintained for 10 h. The relative humidity of the reactor was less than 1% for the dry condition and 70% for the humid ones.

After the toluene combustion experiment, temperature programmed oxidation (TPO) was subsequently conducted in order to identify the amount of carbon species remaining on the catalyst surface as a result of molecular adsorption of toluene and its partial oxidation. Each TPO experiment was conducted from 150 °C to 500 °C with a ramping rate of 1 °C/min under a constant dry air flow of 5 sccm.

Temperature programmed desorption (TPD) experiments were also carried out in order to evaluate the toluene uptake under dry and humid condition. 0.1 g of each sample was outgassed at 500 °C for 90 min and the samples were cooled to 30 °C. The outgassed

Table 1
Experimental parameters used for ALD of NiO and TiO_2 are summarized.

	NiO ALD process		TiO_2 ALD process	
Precursors	$Ni(Cp)_2$ at 200 mtorr	O_2 at 1.3 torr	TTIP at 400 mtorr	H_2O at 400 mtorr
Precursors exposure time	230 s	40 s	42 s	50 s
N_2 purging time	30 s		20/30 s	
Pumping time	60 s		40/60 s	
Substrate temperature	260 °C		150 °C	
Reactor base pressure	10 mtorr		10 mtorr	

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samples were exposed to toluene-containing dry/humid air at 30 °C for 12 h and, prior to each TPD experiment, weakly adsorbed species on the sample surface were removed under a constant flow of dry air for 4 h at room temperature. Subsequently, the temperature of the reactor was raised from 30 to 210 °C at a rate of 1 °C/min. Note that except for the outgassing step, all the TPD process was carried out under a flow of N_2.

3. Results and discussion

3.1. Characterization of catalysts

Si 2p, Ni 2p and Ti 3p core level spectra of XPS of NiO/SiO_2 and $NiO/TiO_2/SiO_2$ are displayed in supporting information 1. On both catalysts, broad Ni 3p peaks corresponding to the mixture of variously oxidized species of Ni (NiO, $Ni(OH)_2$, and Ni_2O_3) were observed, and for $NiO/TiO_2/SiO_2$ catalyst, Ti 2p and 3s peaks corresponding to the Ti(IV) could be observed. In order to obtain more quantitative information of the amounts of NiO and TiO_2 deposited on SiO_2, ICP-OES analyses were carried out, and as summarized in Table 2, Ni contents for both samples were nearly identical (~ 2%). Content of Ti in the $NiO/TiO_2/SiO_2$ sample was determined to be ~ 3%.

In order to obtain information of the surface areas and pore sizes of the catalysts, BET and BJH analyses were carried out. The BET surface area of SiO_2 was slightly decreased from 293.9 m^2/g to 280.0 m^2/g upon NiO deposition whereas no significant difference was observed in the average pore size (SiO_2: 13.9 nm, NiO/SiO_2: 13.5 nm). In the case of $NiO/TiO_2/SiO_2$, the BET surface area and the pore size were 265.3 m^2/g and 12.6 nm, respectively, and these values are both only slightly lower than those of bare and NiO-deposited SiO_2. It is confirmed that the highly porous nature of SiO_2 was maintained after the ALD of either NiO or TiO_2 and NiO.

In order to reveal the structure of NiO/SiO_2 and $NiO/TiO_2/SiO_2$ catalysts, STEM images were obtained. In Figure 2, STEM images of NiO/SiO_2 (a) and $NiO/TiO_2/SiO_2$ (b), respectively, are displayed. In all images, randomly distributed dark spots with an average size less than 2 nm could be found, and EDS analysis revealed that these dark spots correspond to the NiO particles (data not shown). Note that the deposition of TiO_2 does not result in the formation of nanoparticles but thin layers and therefore, it was difficult to identify TiO_2 in STEM (supporting information 2) [40,41]. We can conclude that NiO was deposited in the form of nanoparticles with similar mean particle sizes on both bare and TiO_2-deposited SiO_2.

3.2. Toluene combustion over NiO/SiO_2 catalysts

In order to study the humidity effect on the toluene combustion catalyzed by the NiO/SiO_2 catalyst, the toluene removal efficiency and CO_2 generation over NiO/SiO_2 were analyzed at two different temperatures, 250 and 350 °C, under dry and humid conditions, respectively. The removal efficiency of toluene and the selectivity towards CO_2 were calculated by the following equations;

$$\text{toluene removal}\,(\%) = \frac{[Toluene]_{in} - [Toluene]_{out}}{[Toluene]_{in}} \times 100 \qquad (1)$$

$$CO_2 \quad \text{selectivity}\,(\%) = \frac{[CO_2]\ in\ \ toluene\ \ combustion}{([Toluene]_{in} - [Toluene]_{out}) \times 7} \times 100 \qquad (2)$$

Table 2
Surface areas and mean pore sizes of bare SiO_2, NiO/SiO_2 and $NiO/TiO_2/SiO_2$ are summarized.

	BET surface area (m^2/g)	Average pore size (nm)	Ni atomic %	Ti atomic %
Bare-SiO_2	293.9	13.9	–	–
NiO/SiO_2	280.0	13.5	2.06	–
$NiO/TiO_2/SiO_2$	265.2	12.6	2.22	2.98

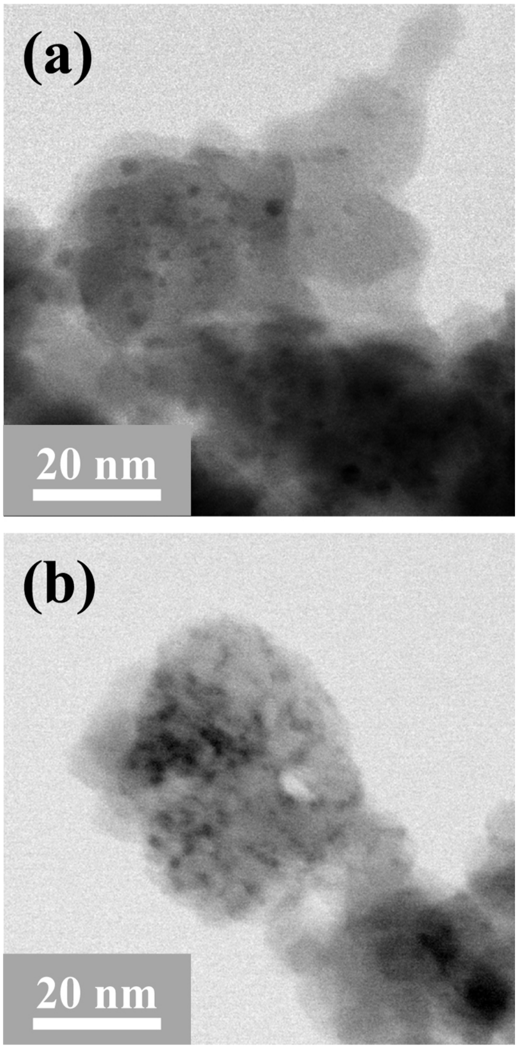

Figure 2. STEM images of NiO/SiO_2 (a) and $NiO/TiO_2/SiO_2$ (b), respectively, are displayed.

At the reaction temperature of 350 °C (Figure 3 (a-c)), all the toluene molecules in the feed stream were nearly completely removed and converted to CO_2 under dry conditions (the CO_2 selectivity = ~ 95%). Desorption of CO_2 was observed during the successive TPO experiments, indicating that a small amount of carbon residues remained on the surface of NiO/SiO_2 during the toluene oxidation experiments. On the other hand, under humid conditions, the toluene conversion was slightly decreased to 92%, but all of the removed toluene molecules were converted to CO_2 (the CO_2 selectivity = ~ 100%), and therefore, no CO_2 molecules were detected in the post-TPO experiment. One can find both positive and negative effects of the humidity on the catalytic activity: the reduction in the toluene conversion of NiO/SiO_2 by the humidity can be a result of the competitive adsorption of toluene and water molecule; water molecule in the reaction system strongly interacts with hydrophilic SiO_2 and block the adsorption of toluene on the catalyst surface. Note that the adsorption of toluene on the substrate surface and subsequent diffusion to the NiO catalystic particles can be an important path for the catalytic oxidation of toluene [42–45]. On the other hand, water molecules can more efficiently dissociatively chemisorb on the surface of catalysts than O_2, and therefore, act as more strong oxidizing agent of toluene than O_2,

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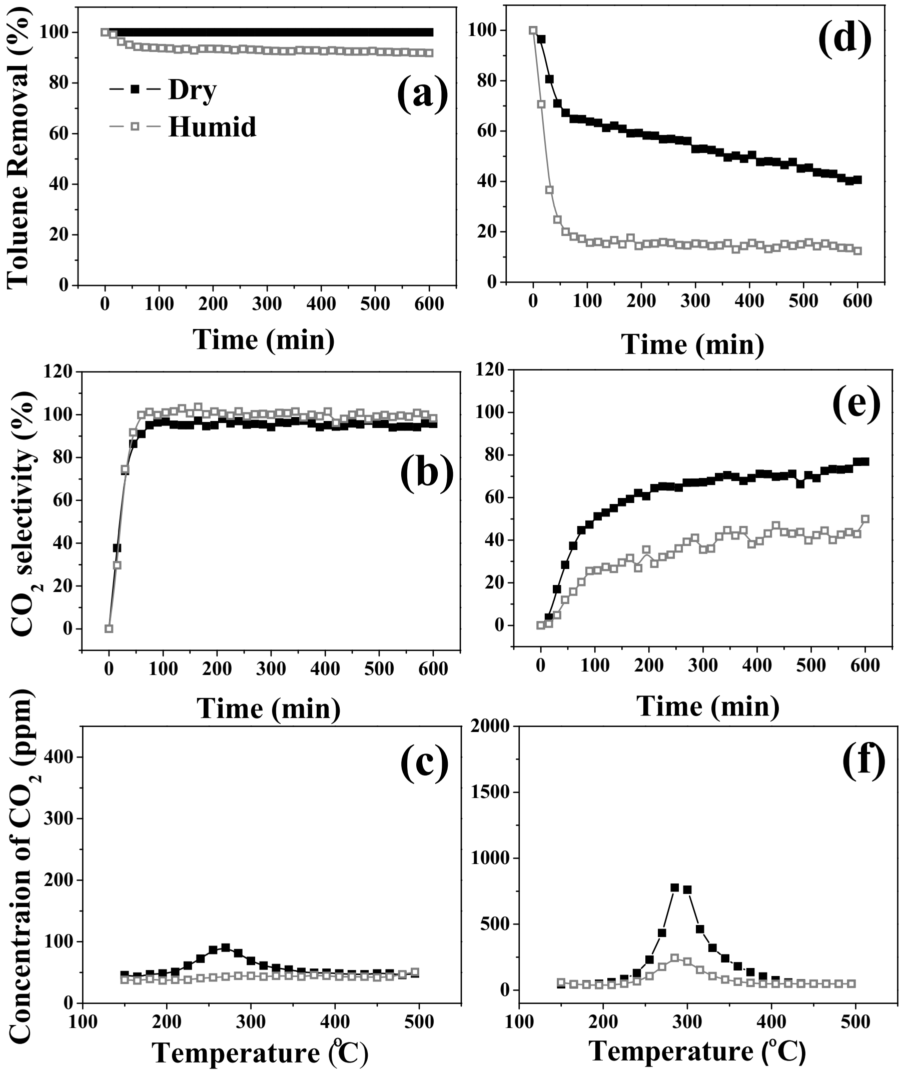

Figure 3. Results of the toluene oxidation catalyzed by NiO/SiO$_2$ are displayed. a-c are the toluene removal efficiency, the CO$_2$ selectivity, and the post-TPO results of the experiments performed dry and humid conditions at 350 °C whereas d-f those of 250 °C.

and this can result in the enhanced CO$_2$ selectivity in the presence of water molecules in the atmosphere.

At the lower reaction temperature (250 °C), both the toluene removal efficiency and the selectivity towards CO$_2$ were decreased compared to the respective values of 350 °C (Figure 3 (d-f)). Under dry conditions, the toluene removal efficiency, which was initially nearly 100%, gradually decreased with increasing reaction time and became ~ 40% after 10 h. At the initial stage of the experiment, the CO$_2$ selectivity was 0%, and this value increased to ~ 65% after 10 h. At the beginning of the reactivity experiment, toluene molecularly adsorbed and at most partially oxidized and remained on the surface, and with increasing reaction time, number of toluene molecules, converted to CO$_2$ and subsequently desorbed, increased. The CO$_2$ selectivity at 250 °C is much lower than that at 350 °C under dry conditions. It is obvious that toluene removal at the lower temperature is occurred as a result of molecular adsorption and partial oxidation of toluene, whereas at the higher temperature, total oxidation of toluene CO$_2$ is much more dominant. The result of the TPO experiment carried out after the reactivity experiment 250 °C under dry conditions showed a higher amount of CO$_2$ desorption than that of 350 °C due to a lower CO$_2$ selectivity at the lower temperature, remaining more carbon residues at 250 °C.

Regarding the effect of the humidity at 250 °C, the reduction in the toluene removal efficiency by the presence of water molecule was much more pronounced compared to that of 350 °C. A lower reaction temperature allows a more facile adsorption of water molecule on the catalyst surface resulting in much more reduced toluene uptake on the catalyst surface and catalytic activity. It is also worth noting that at 250 °C, not only the toluene removal efficiency but also the CO$_2$ selectivity and amounts of residual carbon estimated by the post-TPO result were decreased upon increase in the humidity during the reaction. Generally speaking, increase in the humidity is detrimental to the catalytic activity of NiO/SiO$_2$ at 250 °C.

3.3. Toluene combustion over NiO/TiO$_2$/SiO$_2$ catalysts

A series of toluene combustion experiments were carried out using NiO/TiO$_2$/SiO$_2$ at two different temperatures (250 and 350 °C) under dry and humid conditions, respectively. At the reaction temperature of 350 °C (Figure 4 (a-c)), NiO/TiO$_2$/SiO$_2$ catalyst showed almost identical catalytic performances under dry and humid conditions; toluene removal efficiency of 97% and CO$_2$ selectivity of 96% were observed without deactivation and the TPO results

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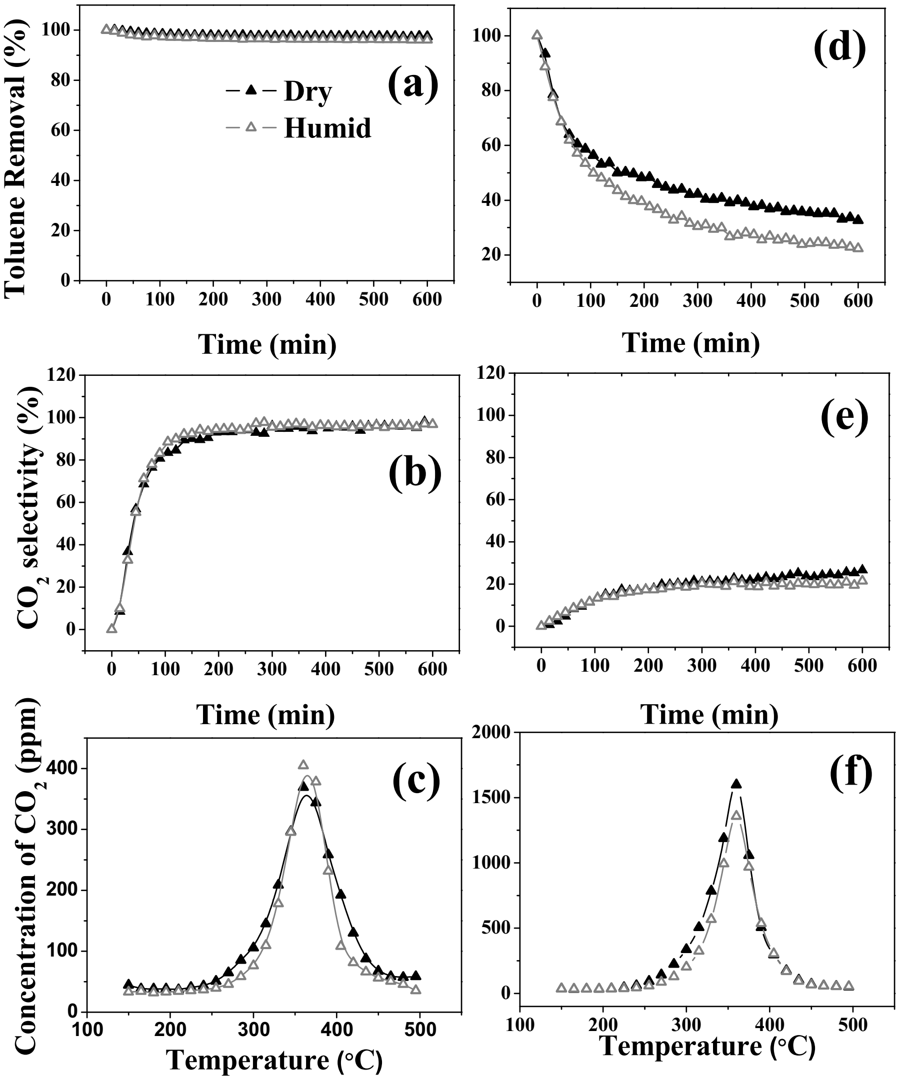

Figure 4. Results of the toluene oxidation catalyzed by $NiO/TiO_2/SiO_2$ are displayed. a-c are the toluene removal efficiency, the CO_2 selectivity, and the post-TPO results of the experiments performed dry and humid conditions at 350 °C whereas d-f those of 250 °C.

were also similar. At 250 °C (Figure 4 (d-f)), the toluene removal efficiency was initially ~ 100%, and this value gradually decreased with time reaching 33% and 22% after 10 h under both dry and humid conditions, respectively, and the CO_2 selectivity was about 20% under both conditions. The TPO area of $NiO/TiO_2/SiO_2$ after the combustion experiment under dry conditions was analogous to those of humid conditions for both reaction temperatures.

Generally, $NiO/TiO_2/SiO_2$ showed lower catalytic activity in terms of the toluene removal efficiency and the CO_2 selectivity compared to NiO/SiO_2 under dry conditions. However, there could be an advantage of use of the TiO_2-layer, when the catalysts are operated under highly humid conditions: the toluene removal efficiency was reduced in the presence of water vapor particularly at the lower temperature using NiO/SiO_2 as catalyst, and the presence of additional TiO_2 layer made the catalysts less influential to the humidity. The $NiO/TiO_2/SiO_2$ catalyst showed higher toluene removal efficiency than NiO/SiO_2 at 250 °C under the highly humid conditions. Answer to the question which catalysts between $NiO/TiO_2/SiO_2$ and NiO/SiO_2 is more active for toluene oxidation is dependent of the experimental conditions such as temperature and humidity; however, one can say that the existence of the TiO_2-layer in the catalysts induces more stable catalytic performances under various humidity conditions.

3.4. TPD results

In order to shed light on the origin of the superior humidity-resistivity of $NiO/TiO_2/SiO_2$, toluene TPD experiments were carried out and the result were compared with that of bare-SiO_2 and NiO/SiO_2 (Figure 5 (a, b)). After the samples were exposed to the dry air containing toluene vapor (Figure 5 (a)), the amount of toluene molecules desorbed from the surface increased in the order of bare-SiO_2 < NiO/SiO_2 < $NiO/TiO_2/SiO_2$. Also, as the toluene uptake increased, the desorption temperature also increased. Even though the surface area of SiO_2 decreased, the toluene uptake and desorption energy increased upon deposition of either NiO or TiO_2, indicating that both NiO and TiO_2 have higher affinity toward toluene compared to that of bare-SiO_2. When humid conditions were used for toluene exposure (Figure 5(b)), no toluene desorption peaks could be observed on bare-SiO_2 and NiO/SiO_2 due to more dominant adsorption of water molecules on the surface, preventing adsorption of toluene. On hydrophilic surfaces such as SiO_2, water molecule can strongly adsorb on the surface and block the adsorption of toluene. On the contrary, a significantly large amount of toluene desorbed from the surface of $NiO/TiO_2/SiO_2$ even after toluene exposure under humid conditions. Based on the TPD results, we can conclude that toluene interacts with TiO_2 surface

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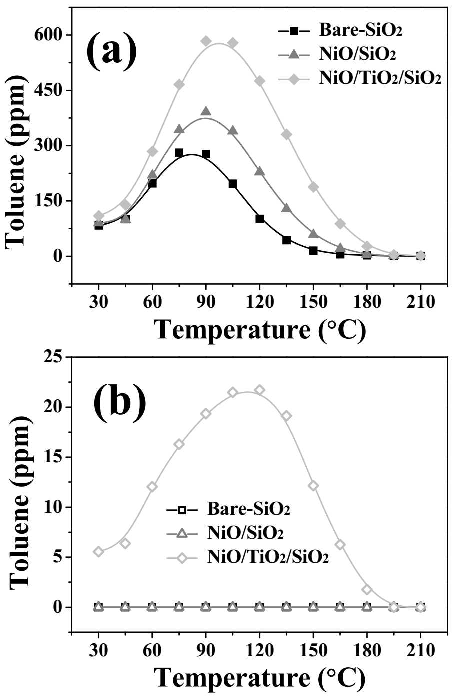

Figure 5. Toluene TPD results after exposure of toluene containing atmosphere a) toluene was exposed with dry air b) Humid atmosphere was used for the toluene exposure.

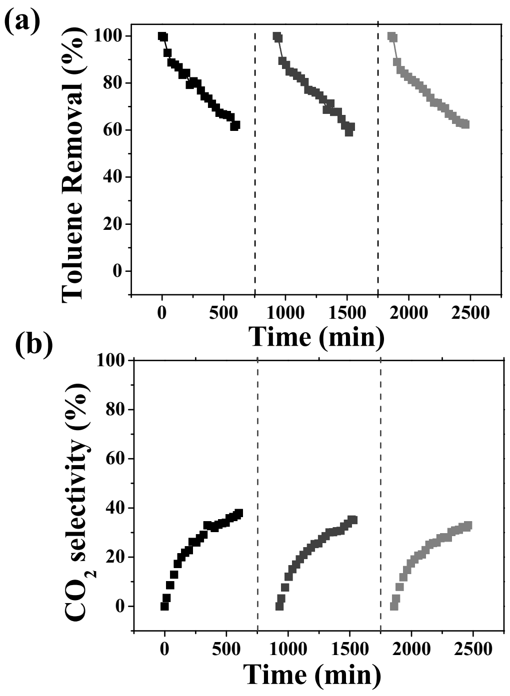

Figure 6. Results of the toluene oxidation experiments at 250 °C under humid conditions and regeneration at 350 °C are displayed.

more strongly compared to NiO or SiO_2, and TiO_2 also has a higher selectivity towards toluene adsorption with respect to water. As a result, $NiO/TiO_2/SiO_2$ can maintain its efficiency for the toluene removal even under humid conditions. It is worth mentioning that the stronger toluene-TiO_2 interaction could be also disadvantageous for the total oxidation of toluene under dry conditions, since the stronger toluene adsorption energy could increase the activation barrier for the total oxidation to CO_2. This suggestion is in line with our observation that TPO areas of $NiO/TiO_2/SiO_2$ were always larger than that from NiO/SiO_2 under all four different experimental conditions, since more carbon residues were formed on $NiO/TiO_2/SiO_2$ than on NiO/SiO_2 during toluene oxidation (Figures 3 and 4).

3.5. $NiO/TiO_2/SiO_2$ regeneration experiment

By using $NiO/TiO_2/SiO_2$ as a catalyst at 250 °C, we can obtain relatively constant toluene removal efficiency upon varying humidity in the feed stream. We made attempts to operate the $NiO/TiO_2/SiO_2$ catalyst at a reaction temperature of 250 °C and occasionally regenerate it by heating to 350 °C. Figure 6 demonstrates the result of repeated toluene combustion over $NiO/TiO_2/SiO_2$ at 250 °C under humid conditions. The initially very high catalytic activity decreased with time, and the catalyst was regenerated every 10 h by heating it to 350 °C under dry air for an hour. The combustion experiment was repeated for 3 times and the regeneration step always fully recovered the initial catalytic activity. We suggest that the use of $NiO/TiO_2/SiO_2$ catalyst at ~ 250 °C and the regular regeneration process at 350 °C could be efficient for the toluene vapor removal without having much influence of the change in the humidity of the environment on the catalytic activity, and this process could be less energy-consuming than the permanent operation of a catalyst at a higher temperature (for example ~350 °C).

4. Conclusion

NiO/SiO_2 and $NiO/TiO_2/SiO_2$ catalysts were prepared by depositing NiO nanoparticle with and without depositing TiO_2 thin layer in advance on SiO_2 using ALD process. The catalysts were used for toluene combustion under dry and humid conditions at 250 and 350 °C, respectively. Under dry conditions, NiO/SiO_2 had higher catalytic activity compared to that of $NiO/TiO_2/SiO_2$ at both 250 °C and 350 °C of the reaction temperature. Under humid conditions, catalytic activity of NiO/SiO_2 significantly decreased due to the competitive adsorption of toluene with water molecules, whereas $NiO/TiO_2/SiO_2$ maintained most of its catalytic activity even under the presence of water vapor, which is the result of a stronger interaction of toluene with TiO_2 surface than SiO_2. At 250 °C under the highly humid conditions, the toluene removal efficiency of $NiO/TiO_2/SiO_2$ exceeded that of NiO/SiO_2.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2015.03.038

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