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Article

Use of NiO/SiO₂ catalysts for toluene total oxidation: Catalytic reaction at lower temperatures and repeated regeneration

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ABSTRACT

We deposited NiO via atomic layer deposition on mesoporous SiO₂ particles with diameters of several hundred micrometers and a mean mesopore size of ~14 nm. NiO was deposited within the shell region of mesoporous SiO₂ particles with a shell thickness of ~11 nm. We annealed the as-prepared NiO/SiO₂ at 450 and 600 °C, respectively. These two samples were used as catalysts for the uptake of toluene molecules and their oxidative conversion to CO₂. The sample annealed at 450 °C was generally more reactive in toluene uptake and its subsequent conversion to CO₂. When the NiO/SiO₂ annealed at 450 °C was exposed to toluene vapor at 160 °C and then heated to 450 °C, CO₂ was emitted with almost no toluene desorption. We suggest that our catalysts can be used as building blocks for odor removal devices that operate below 200 °C. These catalysts can be regularly regenerated at ~450 °C.

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1. Introduction

Volatile organic compounds (VOCs) such as acetaldehyde, formaldehyde, and benzene and its derivatives (such as toluene) can cause sick-building syndrome. There has been much concern about high VOC levels inside new buildings and automobiles [1–4]. VOCs can also be emitted from automobiles into the atmosphere as a result of incomplete fuel conversion. The control of VOCs is therefore important in both indoor atmospheres and outdoors [1–7]. Among various VOCs, benzene and its derivatives are regarded as the most difficult chemical species to oxidize completely to non-harmful molecules [8–10].

There are a number of technical developments that can be used to remove high VOC levels from the atmosphere.

High-surface-area materials such as activated carbon can be used to remove VOCs; however, they need to be regularly replaced or regenerated because they lose their ability to remove VOCs once their surface sites have been saturated with molecules [11–14]. When the used adsorbents are regenerated, VOCs can be re-emitted into the air, causing secondary pollution of the atmosphere [10,14]. Additionally, under highly humid conditions, the surfaces of these materials can become saturated with water molecules, reducing VOC uptake [10,15,16]. Photocatalysts can also be used to remove VOCs; however, in practice, air purification via photocatalysis is challenging because of catalyst poisoning, i.e., photocatalytic activity is lost with time because of the occupation of surface reaction sites by reaction intermediates [2,17–21].

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Oxidation catalysts can also be used under dark conditions to facilitate oxidative reactions of VOCs with O₂ and H₂O to form CO₂ and H₂O. Nanoparticles of Pt-group metals such as Pt [16,22–25], Pd [26], and Rh [27] supported on porous oxides with high surface areas can be used as catalysts for the oxidation of VOCs. However, alternatives to these materials are needed because of their high cost and scarcity. Catalysts based on less expensive materials such as Co [27–31], Ni [2,9,10,32,33], and Mn [3,15,34–37], with various structures and dopant addition, have been suggested as materials for the efficient catalysis of oxidative reactions of VOCs [38,39].

VOC oxidation catalysts should have high initial activities and the activity must be sustained for an extended period of time. Small nanoparticles (less than ~5 nm) are highly efficient catalysts for VOC oxidation because of their high surface-to-volume area and their large number of catalytically active under-coordinated sites. However, they often suffer from sintering [8,40–50], resulting in significant reductions in their catalytic activities with increasing reaction time. Incorporation of catalytically active nanoparticles into a mesoporous substrate could solve this problem; however, the insertion of nanoparticles deep into the mesopores of a substrate is difficult. Atomic layer deposition (ALD), in which a cycle of alternating exposures to reactive precursors, with purging and pumping between exposures to different precursors, is an effective method for incorporating metal or metal oxide nanoparticles into the mesoporous structures of substrates [8,9,46,51–66]. Catalysts for various reactions prepared using ALD have been reported recently; they have high stabilities under various reaction conditions [8,9,46,54,56,57,63,65,66].

In the present work, we investigated the toluene oxidation activity of NiO deposited via ALD on mesoporous SiO₂. We show that these catalysts can be used at ~160 °C and regularly regenerated at 450 °C; their catalytic activities in the total oxidation of toluene vapor can therefore be sustained.

2. Experimental

2.1. Sample preparation

NiO/SiO₂ catalysts for toluene oxidation were prepared using ALD. Bis(cyclopentadienyl)nickel [Ni(Cp)₂; Aldrich] and O₂ (99.99%) were used as precursors for NiO particle deposition on a mesoporous SiO₂ substrate (mean pore size = 13.8 nm, 35–60 mesh, Aldrich). The temperatures of the bottle containing the Ni(Cp)₂ precursor and the substrate were maintained at 60 and 260 °C, respectively, during NiO deposition. The Ni(Cp)₂ precursor was injected into the chamber for 200 s with a working pressure of 250 mTorr (pulsing step). The substrate, which was located in the center of the chamber, was exposed to the injected Ni(Cp)₂ precursor for 30 s (exposure step). After the Ni(Cp)₂ pulsing and exposure steps, the O₂ precursor was injected into the chamber for 10 s with a working pressure of 1.2 Torr; this remained in the chamber for a 30 s exposure step. The chamber was purged by injection of N₂ (99.99%) gas immediately after exposure to each precursor; this was pumped out using a rotary oil pump. After each pumping step, the base

pressure of the chamber was maintained below 10 mTorr. One cycle of NiO deposition on the substrate consisted of these processes. In this work, 50 ALD cycles were applied to the SiO₂ substrate.

2.2. Toluene adsorption experiments

Toluene was oxidized over the 50-cycle NiO/SiO₂ catalyst in a continuous-flow quartz fixed-bed reactor (internal diameter = 21 mm, length = 300 mm) at atmospheric pressure. The experimental set-up consisted of a mass flow controller (MFC) for dry air, a bottle filled with liquid toluene, a furnace, a quartz reactor, and an on-line gas chromatography (GC) system (HP6890, Hewlett Packard). A schematic diagram of the experimental set-up can be found in Ref. [2]. The composition of the gas mixture was determined every 15 min using an on-line GC system equipped with a capillary column (HP-5, 30 m × 0.32 mm, Agilent Technologies), a methanizer, and a flame ionization detector. The sample (1.1 g) was loaded into a quartz holder (15 mm × 70 mm × 5 mm), which was placed in the center of the reactor. Before each toluene adsorption experiment, the NiO/SiO₂ sample was annealed at either 450 or 600 °C for 2 h under dry air.

The NiO nanoparticle size and the level of carbon impurities on the NiO surface are influenced by the pre-annealing temperature, and both can alter the catalytic activity of a nano-sized catalyst [41,50,67,68]. The catalytic activity of a nano-sized catalyst decreases with increasing nanocatalyst particle size, and increases with decreasing amount of carbon impurities [41,50,67,68]. Our previous study showed that the NiO nanoparticle size increased and the carbon impurity level on the NiO surface decreased with increasing pre-annealing temperature in the range 300–750 °C [8]. There was therefore an optimum pre-annealing temperature range, and NiO/SiO₂ samples pre-annealed at 450 and 600 °C showed high catalytic activities in CO oxidation [8]. Here, we pre-annealed the NiO/SiO₂ samples at these two temperatures to optimize the effects of the pre-annealing process on the catalytic activity of the NiO nanoparticles.

Bare and NiO-deposited SiO₂ samples were pre-annealed at 450 °C for 2 h. After pre-annealing, the quartz reactor was cooled to one of three temperatures, i.e., 60, 100, or 160 °C; this temperature was kept constant during the toluene uptake experiment (breakthrough curve measurements). The flow rate of dry air containing toluene vapor (95 ppm) was maintained at 10 standard-state cubic centimeter per minute (sccm) by the MFC. After the breakthrough curve of each sample showed saturation, temperature-programmed oxidation (TPO) analysis was conducted to determine the amounts of toluene and other carbon-containing residues remaining on the sample surface. Before each TPO analysis, N₂ gas was flowed into the reactor at a rate of 50 sccm for 1 h to remove any weakly (or reversibly) bound toluene from the sample surface, and the amount of weakly bound toluene species was quantified. During the N₂ flow process, the temperature of the quartz reactor was kept the same as the corresponding temperature in the breakthrough analysis; each TPO experiment was started by dry air

injection after stopping the N₂ flow. In the TPO experiments, dry air was flowed into the reactor at 10 sccm. The reactor temperature was increased at 1 °C/min from the breakthrough experiment temperature to 450 °C. In addition, for NiO/SiO₂ pre-annealed at 450 °C, a toluene oxidation experiment at 100 °C for 10 h was repeated three times and the sample was annealed at 450 °C for 2 h in dry air before each toluene breakthrough experiment. This was done to regenerate the adsorption capacity and catalytic activity of the sample. No species other than toluene and CO₂ were detected by on-line GC in any of the experiments performed with the NiO/SiO₂ samples. This indicates that there were no secondary pollutants in the gas phase, e.g., formaldehyde or acetaldehyde generated during heating to a high temperature (450 °C).

2.3. Sample characterization

The elemental composition of the 50-cycle NiO/SiO₂ was determined using inductively coupled plasma optical emission spectroscopy. N₂ adsorption-desorption isotherms of the bare and NiO-deposited SiO₂ were obtained using a gas sorption analyzer (3Flex, Micromeritics) and the surface areas and mean pore sizes of the two samples were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. The samples were degassed at 450 °C for 2 h before the N₂ adsorption experiments. The chemical states and compositions of the sample surfaces were investigated using X-ray photoelectron spectroscopy (XPS). The ultra-high vacuum (UHV) main chamber (base pressure 2.0 × 10⁻¹⁰ Torr) for the XPS measurements was equipped with a monochromatic X-ray source (Mg K α , 1253.6 eV) and a concentric hemispherical analyzer (CHA, PHOIBOS-Hsa 3500, SPECS). NiO/SiO₂ samples were pre-annealed under a dry-air flow in a reactor inside a glove box filled with Ar gas, and then the samples were transferred to the UHV system, using a vacuum-sealed transfer system, without air exposure. This transfer system enables the effects of possible surface contamination or changes caused by air exposure to be excluded from the surface analysis results. The XP spectra were recorded at a pass energy of 30 eV. The intensities of the XPS peaks (Ni 2p, O 1s, and C 1s) of both samples (bare and NiO-deposited SiO₂) were normalized by the respective Si 2p peak intensity, and the binding energies were calibrated based on the C 1s peak position (binding energy $\approx$ 284.5 eV). Energy-dispersive spectroscopy with scanning electron microscopy (SEM; JSM-7100F, JEOL) was used to determine the elemental composition of NiO/SiO₂. Transmission electron microscopy (TEM; JEM-ARM200F, JEOL) was used to determine the size of the NiO particles on NiO/SiO₂. For TEM analysis, the NiO/SiO₂ samples were ground, pre-annealed at 450 and 600 °C, dispersed in ethanol, and then dropped on a Cu grid. High-angle annual dark field images were obtained at an electron acceleration voltage of 200 kV. The optical properties of the samples were studied using ultraviolet diffuse-reflectance spectroscopy (UV-DRS; UV-3600, Shimadzu).

3. Results and discussion

Table 1

Ni content, BET surface area and average pore diameter of the bare SiO₂ and 50-cycled NiO/SiO₂.

Sample	Ni content (wt%)	S _{BET} (m ² /g)	Average pore diameter (nm)
Bare SiO ₂	0.0	297.7	13.8
50-cycled NiO/SiO ₂	2.9	302.6	13.4

Table 1 shows the elemental compositions, surface areas, and mean pore diameters of the bare and 50-cycle NiO/SiO₂ samples. After 50 cycles of NiO ALD, the Ni content of the sample had increased from 0% to 2.9% [8,46,54]. NiO deposition did not greatly change the surface area (estimated using the BET method) and mean pore diameter (determined using the BJH method). This is probably because of the small NiO loading achieved using ALD [8–10,46,54,57].

We fractured the 50-cycle NiO/SiO₂ and studied its fringe using SEM with an elemental-imaging technique to investigate the deposited Ni distribution in a mesoporous SiO₂ particle of diameter several hundred micrometers. Fig. 1 shows that Si from the substrate was evenly distributed over the entire sample (the right-hand part of Fig. 1(a)), whereas Ni was only present in the shells of the SiO₂ particles [8]. The depth of the region in which Ni was detected was $\sim$ 11 nm. We suggest that the thickness of the Ni-containing shell is limited by the diffusion length of the nickelocene precursor inside the mesoporous SiO₂ during the ALD process. These results are similar to those reported for the penetration depth of Pt in carbon aerogel structures [69].

In the present work, we used two different pre-annealing temperatures (450 and 600 °C) prior to each catalytic activity test of the ALD-prepared catalysts. The samples were examined using XPS to elucidate the changes in the chemical compositions and states of the catalyst surfaces caused by pre-annealing at the two temperatures (Fig. 2). Fig. 2(a) shows that the Ni 2p_{3/2} spectrum consisted of two broad peaks centered at $\sim$ 856 and $\sim$ 862 eV. The higher binding energy shoulder can be attributed to the Ni 2p_{3/2} satellite arising from the shake-up process [70,71]. The main feature of the Ni 2p_{3/2} spectrum is the absence of the peak for metallic Ni at $\sim$ 853 eV [72]. The experimentally observed features are a mixture of NiO peak at $\sim$ 854 eV and Ni(III) (Ni₂O₃, NiOOH) peak at $\sim$ 856 eV [70,71]. We conclude that Ni was not present in its metallic form but was present in various oxidized forms. The annealing temperature had almost no effect on the chemical compositions and oxidation states of the catalysts. However, the Ni/Si inten-

Fig. 1. EDS mapping images of the (a) Si and (b) Ni K series from the mechanically fractured NiO/SiO₂ catalyst.

Fig. 2. (a) Ni 2p, (b) Si 2p, and (c) O 1s XPS spectra of the NiO/SiO₂ pre-annealed at 450 and 600 °C, respectively.

sity ratio, calculated from the respective XPS peak areas, decreased from 0.58 to 0.54 as the pre-annealing temperature increased from 450 to 600 °C. It is important to note that XPS is a surface sensitive analytical technique, and only a depth of 3–5 nm from the top surface can be examined using XPS. The results imply that NiO nanoparticles aggregated at the higher temperature, forming larger nanoparticles, and this lowered their surface-to-volume ratio. The dissimilarities of the Si 2p and O 1s core-level XP spectra of the samples prepared at different pre-annealing temperatures confirm that the NiO nanoparticles size increased with increasing pre-annealing temperature from 450 to 600 °C. The Si 2p core-level peak shifted to higher binding energy as the pre-annealing temperature increased from 450 to 600 °C (Fig. 2(b)). Charge transfer from Ni to Si can occur at the Ni-Si interface; this is known as metal-to-support charge transfer and this additional charge on Si (SiO₂) can reduce the binding energy of the Si 2p core level. The amount of metal-to-support charge transfer decreased with increasing mean NiO nanoparticle size as the pre-annealing temperature increased from 450 to 600 °C, resulting in an increase in the binding energy of the Si 2p core-level peak. The lower-binding-energy shoulder (~530 eV) in the O 1s core-level spectra (Fig. 2(c)) is attributed to the oxygen in NiO, whereas the main O 1s peak (~532 eV) is attributed to SiO₂ [72]. The relative intensity of this lower-binding-energy shoulder (~530 eV) to that of the main O 1s core-level peak (~532 eV) decreased with increasing pre-annealing temperature; this is in line with the decrease in the Ni/Si XPS peak ratio for the sample pre-annealed at a higher temperature (600 °C).

It is difficult to determine the lateral size of the NiO nanoparticles precisely because of the low contrast between Ni and Si in the TEM image; the mean NiO particle size after annealing at 600 °C does appear to be slightly larger (related data can be found elsewhere [8]). The mean particle sizes in both cases were estimated to be less than ~2 nm. Our UV-Vis absorption spectroscopy data show more clearly that the mean particle size of the sample annealed at 600 °C was larger than that of the sample annealed at 450 °C. The 450 °C-annealed sample showed a blue shift of its visible absorption peak with respect to that of the 600 °C-annealed sample. The absorbance spectra in Fig. 3 were obtained by transforming the reflectance data

using the Kubelka-Munk function for diffused reflectance. Note that the optical absorption at around ~400 nm can be attributed to Ni(II) species in the SiO₂ network. A red shift should appear with increasing particle size [8]. The results shown in Fig. 3 suggest that pre-annealing at the higher temperature increased the particle size.

Although there are only subtle differences between the structural properties and chemical compositions of the NiO/SiO₂ catalysts annealed at 450 and 600 °C, these two samples showed very different catalytic activities. Fig. 4 shows the breakthrough curves for toluene vapor diluted with dry air for 50-cycle NiO/SiO₂ samples pre-annealed at 450 and 600 °C. The toluene breakthrough experiments for each sample were conducted at three different reactor temperatures (60, 100, and 160 °C). In each breakthrough curve, a toluene signal is not visible at the beginning of the experiment using a gas chromatograph connected to the end of the reactor. This is because all the toluene vapor that passed through the reactor inlet was captured by the samples (by simple molecular adsorption or partial oxidation) and was subsequently attached to the surface. As the reaction time increased, the toluene uptake rate decreased and toluene vapor was detected at the reactor outlet. The toluene vapor pressure gradually increased and finally reached a specific value at the inlet, i.e., at this stage, no more toluene uptake occurred. The amount of toluene that was re-

Fig. 3. UV absorption spectra of the NiO/SiO₂ pre-annealed at 450 and 600 °C, respectively.

Fig. 4. Toluene breakthrough curves of (a) 450 °C-annealed and (b) 600 °C-annealed NiO/SiO₂ at various reaction temperatures. (c) Toluene uptake capacities of the bare SiO₂, 450 °C-annealed and 600 °C-annealed NiO/SiO₂ at various reaction temperatures.

moved by the sample in the reactor can be determined from the breakthrough curve.

For bare SiO₂, the toluene uptake was fairly high, at 60 °C; however, as the sample temperature during the breakthrough experiment increased, the toluene uptake decreased significantly (Fig. 4(c)). This result is typical of simple molecular adsorption of toluene. Molecular adsorption is generally exothermic, therefore increasing the temperature decreases the amount of toluene that is adsorbed on the surface of a solid substrate. For the NiO/SiO₂ samples annealed at 450 and 600 °C, the toluene uptake also decreased with increasing temperature. However, in these cases, toluene could still be removed to some extent at 160 °C. These results differ greatly from those for bare SiO₂, which lost most of its toluene uptake capacity by ~100 °C. This implies that there is another channel for toluene uptake at higher temperatures (100 and 160 °C) for the NiO/SiO₂ samples annealed at 450 and 600 °C. It has been reported that toluene can be partially oxidized over NiO nanoparticles above 100 °C to benzaldehyde and benzoic acid [73–76], therefore another toluene uptake channel is probably available in the presence of NiO nanoparticles (NiO/SiO₂ sample) at 100 and 160 °C.

Fig. 5. Pore size distribution curves of bare SiO₂, 450 °C-annealed and 600 °C-annealed NiO/SiO₂. Calculated BET surface area of bare SiO₂, 450 °C-annealed and 600 °C-annealed NiO/SiO₂ (inset).

It is worth noting that the total toluene uptake capacity at 60 °C was almost the same for bare SiO₂ and NiO/SiO₂ annealed at 450 °C; however, the toluene uptake capacity at 60 °C of the sample annealed at 600 °C was significantly lower. BET and BJH analyses (Fig. 5) show that there was almost no change in the surface areas, pore volumes, or pore size distributions of these three samples. It can therefore be argued that a subtle difference in the structure of the NiO particles in the NiO-containing samples significantly changed the chemical activity.

A TPO experiment was performed (Fig. 6) after each breakthrough experiment shown in Fig. 4. For the NiO/SiO₂ sample pre-annealed at 450 °C, the symmetric CO₂ evolution peak centered at ~300 °C became larger as the breakthrough temperature increased. Additionally, the evolution temperature decreased as the CO₂ evolution peak increased (Fig. 6(a)). After the breakthrough experiment at 60 °C, a broad molecular desorption peak for toluene (centered at 130 °C) was observed (Fig 6(b)). This peak became smaller as the temperature of the breakthrough experiment increased until almost no toluene desorption was observed (in the breakthrough experiment at 160 °C).

In the case of the 600 °C-annealed sample, the CO₂ evolution and toluene desorption peaks were both generally smaller than those for the 450 °C-annealed sample; this is in agreement with the lower toluene uptake of the 600 °C-annealed sample, shown in Fig. 4(c). It is also important to note that the center of the CO₂ evolution peak was at 325 °C when the breakthrough experiment (prior to the TPO experiment) was performed at 160 °C (Fig. 6(c)). This temperature is significantly higher than the corresponding value for the 450 °C-annealed sample (Fig. 6(a)). In summary, the toluene uptake and CO₂ conversion efficiency for the 450 °C-annealed sample were superior to those of the 600 °C-annealed sample for the same toluene vapor exposure and subsequent heating under an air stream. There seems to be a significant particle size effect on the toluene oxidation reactivity of NiO nanostructures on SiO₂ (for particles smaller than ~2 nm). Further studies are needed to determine the origin of this size effect.

Fig. 7(a) and (b) quantitatively compare the TPO data in Fig.

Fig. 6. CO₂ evolution of the (a) 450 °C-annealed and (c) 600 °C-annealed NiO/SiO₂ samples, and toluene desorption of the (b) 450 °C-annealed and (d) 600 °C-annealed samples during TPO experiments.

6 with those for the weakly bound toluene species that were desorbed before each TPO experiment started. For the 450 °C-annealed sample, the number of weakly bound toluene species removed before each TPO experiment and the number of more strongly bound toluene species desorbed at ~130 °C decreased as the breakthrough experiment temperature increased. At the same time, the CO₂ evolution peak increased in intensity (Fig. 7(a)). Toluene and CO₂ were the only species detected by GC during the TPO experiments. The result was similar for the 600 °C-annealed sample (Fig. 7(b)). We also tried to stop the breakthrough experiment with the 450 °C-annealed sample when reaction time was ~30% of the time required for saturation of the breakthrough curve. TPO experiments were then performed at this point (Fig. 7(c)). As shown in Fig. 7(c), almost no weakly bound toluene species were identified. As the temperature of the breakthrough curve measurements increased, toluene desorption became less pronounced and CO₂ evolution increased. After the breakthrough experiment at 160 °C, almost 100% emission of CO₂ (without any other molecules) was observed. The CO₂ selectivities of stored toluene (except for weakly bound toluene) on the two NiO/SiO₂ samples (annealed at 450 and 600 °C) were calculated using the following equation:

$$\text{CO}_2 \text{ selectivity} = \frac{\text{amount of generated CO}_2}{\text{amount of generated toluene} + \text{amount of generated CO}_2}$$

The calculated CO₂ selectivities of stored toluene (except for weakly bound toluene) on the two NiO/SiO₂ samples in the

TPO experiments were close to 1 (0.99 and 0.98 for 450 °C-annealed NiO/SiO₂ and 600 °C-annealed NiO/SiO₂, respectively).

Our goal is to use our catalyst at lower temperatures to reduce energy consumption. We also want to obtain a catalyst that only occasionally needs to be regenerated at higher temperatures. The emission of harmful molecules during regeneration should also be minimized. We have shown that these goals can be achieved using NiO/SiO₂ catalysts, which can be used at 100–160 °C and regenerated at 450 °C. Regeneration of the deactivated catalyst is important in practical applications [8,77]; in our case, the deactivated NiO/SiO₂ catalyst surface can be fully reactivated by increasing the temperature to 450 °C. The carbon residues on the NiO/SiO₂ catalyst surface were removed when the temperature was increased during the TPO experiments and they were completely removed before the temperature reached 450 °C (Fig. 6). We therefore chose 450 °C as the regeneration temperature and checked whether the initial toluene uptake capacity of the fresh NiO/SiO₂ sample can be fully recovered by heating to 450 °C. The NiO/SiO₂ sample pre-annealed at 450 °C was treated with toluene vapor for ~10 h at 100 °C, and then the sample was annealed at 450 °C for 2 h (Fig. 8). The toluene uptake capacity of the regenerated sample was evaluated; it was almost the same as the initial toluene uptake capacity, i.e., annealing at 450 °C achieved full recovery of the original toluene uptake capacity (Fig. 8). Furthermore, the toluene uptake capacity of the sample was fully recovered

Fig. 7. Emitted substances from each sample during the TPO experiments of Fig. 5. (a) and (b) are from the 450 °C- and 600 °C-annealed NiO/SiO₂, respectively; (c) 450 °C-annealed NiO/SiO₂ was exposed to toluene vapor at 100 °C with a reaction time corresponding to 30% of the toluene uptake saturation. The emitted substances after the TPO experiments were analyzed.

after repeated recovery cycles (toluene exposure for 10 h and subsequent annealing at 450 °C), labeled 3rd toluene oxidation in Fig. 8. This indicates that the NiO/SiO₂ catalyst presented in this study has a high resistance to sintering, therefore the toluene removal capability of the NiO/SiO₂ catalyst can be recovered by simple annealing at 450 °C.

We compared the toluene uptake capacities of the NiO/SiO₂ catalyst at 60, 100, and 160 °C with those of recently reported adsorbents (Table 2). It is important to mention that the different experimental conditions (e.g., adsorption temperature and initial concentration of toluene) should be considered when comparing the reported adsorption capacities of various adsorbents. Among the adsorbents listed in the table, phosphoric acid-modified activated carbon (PA/AC) showed the highest toluene adsorption capacity per unit mass of adsorbent (mmol/g). The toluene adsorption capacity of our NiO/SiO₂ sample was lower than that of PA/AC in terms of the amount of adsorbed toluene per unit mass, but the NiO/SiO₂ sample showed a comparable adsorption capacity in terms of toluene uptake per unit area. It should be noted that the adsorption capacity of PA/AC [78] was measured at a lower temperature (25 °C) than in our case (>60 °C). Molecular adsorption is generally exothermic, therefore the amount of toluene ad-

Fig. 8. Results of toluene breakthrough experiments of the 450 °C-annealed NiO/SiO₂ at 100 °C after repeated cycles of breakthrough experiments at 100 °C and regeneration at 450 °C.

sorbed by PA/AC may decrease with increasing adsorption temperature. It is also important to note that the adsorption capacity of our NiO/SiO₂ catalyst can be fully recovered by simple annealing at a higher temperature (450 °C), without pro-

Table 2

The capacities of toluene adsorption of NiO/SiO₂ samples studied here were compared with other adsorbents reported in the literature.

Sample	Surface area (m ² /g)	Adsorption temperature (°C)	Adsorbed amount of toluene (mmol/g)	Adsorbed amount of toluene (mmol/m ²)	[Ref.]
Bare SiO ₂	297.7	60	2.65	0.0089	Current work
450 °C-annealed NiO/SiO ₂	292	60	2.50	0.0086	
450 °C-annealed NiO/SiO ₂	292	100	1.97	0.0067	
450 °C-annealed NiO/SiO ₂	292	160	1.00	0.0034	
PA/AC	1109	25	4.21	0.0038	[78]
Semi-coke	—	20	0.26	—	[79]
SiO ₂ -A	976.5	150	0.21	0.00022	[80]
Ag/SiO ₂ -A	473.1	150	0.26	0.00055	[81]
MCM-41	1154	25	0.29	0.00025	
Q3 (CARIACT Q-3, Fuji Silysia Chemical Ltd.)	725	25	0.16	0.00022	
HY (HSZ-320HOA, Toso Co.)	732	25	0.13	0.00018	
AC (LGH006, Takeda Chemical Industries, Ltd.)	1146	25	0.18	0.00016	

Table 3

The catalytic activities of NiO/SiO₂ samples were compared to other non-noble metal based catalysts in the literature in terms of specific reaction rate, $T_{50\%}$, $T_{90\%}$, and stability.

Sample	Reaction temperature (°C)	Specific reaction rate (mmol/(h·g))	$T_{50\%}$ (°C)	$T_{90\%}$ (°C)	Stability test (at $T_{90\%}$)	Regeneration test	[Ref.]
ALD 50-cycled NiO/SiO ₂	160	0.167	—	—	—	O (3 times)	Current work
ALD 40-cycled NiO/SiO ₂	—	—	220	247	O (10 h)	—	[9]
Co ₃ O ₄ microspheres	150	0.0376	230	254	O (100 h)	—	[29]
Co ₃ O ₄ -HT-CTAB	150	0.164	195	215	O (100 h)	—	[30]
Mesoporous Co ₃ O ₄	150	0.246	—	240	O (24 h)	—	[31]
Mn ₃ O ₄	150	0	245	270	—	—	[34]
LaMnO ₃	150	0.000277	257	298	—	—	[37]

ducing any harmful pollutants in the gas phase. We would like to emphasize that the main goal of our experiments was to investigate the possible use of NiO/SiO₂ catalysts for the removal of harmful pollutants (e.g., toluene) at lower temperatures, with lower energy consumption; we have successfully demonstrated that this is possible.

We also compared the catalytic performances of our NiO/SiO₂ sample with those of other non-novel metal-based catalysts reported in the literature in terms of specific reaction rate (mmol/(h·g)), $T_{50\%}$, $T_{90\%}$, and stability at $T_{90\%}$ (Table 3). Although direct comparison with the catalytic activities of various catalysts reported in the literature is not easy because of the variations in experimental conditions, the catalytic activity of the NiO/SiO₂ catalyst studied here was comparable to those of the catalysts listed in Table 3. It is also worth mentioning that regeneration of the used catalysts and recovery of the original activity (i.e., catalyst stability) have rarely been carefully considered in previous reports, but were tested in the present work.

4. Conclusion

NiO/SiO₂ with 2.9% Ni loading were prepared using ALD. The samples were annealed at 450 and 600 °C, respectively. NiO was deposited in the outermost region of mesoporous SiO₂ microparticles with a shell depth of ~11 nm. In contrast to bare SiO₂, which showed almost no uptake of toluene vapor above 100 °C, NiO/SiO₂ showed significant uptake of toluene (even at 160 °C). This is probably the result of partial oxidation of toluene on the supported NiO and spill-out onto the SiO₂ surface. The toluene uptake efficiency of the 450 °C-annealed sample was considerably higher than that of the 600 °C-annealed sample over a wide range of temperatures. A TPO experiment was performed after each toluene uptake experiment. When the NiO/SiO₂ samples were exposed to toluene vapor at 100 and 160 °C, and then heated to 450 °C, CO₂ evolution was observed. As the temperature of the breakthrough experiment increased, toluene desorption decreased and CO₂ emission increased. The CO₂ conversion efficiency over the 450 °C-annealed sample was higher than that over the 600 °C-annealed sample. Based on our results, we suggest that NiO/SiO₂ can be used at 100–160 °C and regularly regenerated at 450 °C. Almost complete conversion of toluene to CO₂ can be achieved.

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Graphical Abstract

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Use of NiO/SiO₂ catalysts for toluene total oxidation: Catalytic reaction at lower temperatures and repeated regeneration

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NiO/SiO₂ samples were prepared by atomic layer deposition. They exhibited significant toluene uptake capacity (<200 °C) and their toluene removal capacities can be fully regenerated by heating (at 450 °C) without generation of harmful by-products

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更低温度下和重复再生时NiO/SiO₂催化剂上甲苯完全氧化反应

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摘要: 采用原子层沉积法将NiO沉积到粒径约为100 nm、平均孔径为14 nm的中孔SiO₂颗粒的壳层(壳层厚度11 nm)区域, 并分别在450和600 °C进行热处理. 将制得的这两种Ni/SiO₂样品用于催化甲苯分子吸附及其氧化为CO₂的反应中. 结果发现, 在450 °C热处理的样品在甲苯吸附及其随后氧化为CO₂的反应中表现出更高的活性; 当将该样品暴露在160 °C甲苯蒸气中, 然后加热到450 °C时, 排放出CO₂, 而几乎没有甲苯脱附出来. 这表明该催化剂可用于在200 °C以下操作的、用于消除建筑物内有味气体的设备中, 且该催化剂可以在450 °C下经过热处理得到再生.

关键词: 多相催化; 化学吸附; 热脱附; 中孔材料; 甲苯氧化

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