Size-Dependent Strong Metal–Support Interactions of Rutile TiO$_2$-Supported Ni Catalysts for Hydrodeoxygenation of m-Cresol

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Abstract: A series of rutile TiO$_2$-supported Ni catalysts with varying Ni sizes were prepared and reduced at 650 °C to explore the effect of Ni size on the strong metal–support interactions (SMSI) and its consequences on the hydrodeoxygenation (HDO) of m-cresol at 350 °C and atmospheric pressure. When the Ni size increases from 4 to 29.1 nm, the SMSI becomes stronger, e.g., the thickness of the TiO$_x$ overlayer and the coverage extent of TiO$_x$ on the Ni particle surface increase. Direct deoxygenation to toluene is the dominant pathway on Ni/TiO$_2$ catalysts with varying Ni loadings, with almost no CH$_4$ being formed. These results indicate that the TiO$_x$ overlayer significantly alters the property of Ni. That is, the C-C hydrogenolysis activity on bare Ni is completely inhibited due to SMSI, while the deoxygenation activity is improved at the Ni-TiO$_x$ interfacial perimeter sites. Meanwhile, the turnover frequency of HDO on small Ni particles of 4 nm is > 2 times higher than that on large Ni particles of 29.1 nm, indicating that the small Ni particle with moderate SMSI appears to be optimal for the direct deoxygenation of m-cresol to toluene. The results suggest HDO activity may be enhanced by tuning the metal particle size and SMSI degree.

Keywords: Ni/TiO$_2$; rutile; strong metal-support interactions; m-cresol; hydrodeoxygenation

1. Introduction

Oil, coal, and natural gas are not only non-renewable but also face shortages and depletion since energy consumption is ever-growing. At the same time, burning fossil fuels may cause environmental pollution, such as global warming, acid rain, and ozone layer depletion. Therefore, the development of clean and renewable energy sources instead of fossil fuels is the key to solving the energy problem. Fast pyrolysis effectively converts lignin biomass into phenolic-rich bio-oil [1–3], which can be converted to chemicals and fuel components by a hydrodeoxygenation (HDO) reaction [4–6]. Among different routes that likely happen during HDO, the direct deoxygenation (DDO) route consumes a minimal amount of H$_2$ and produces aromatics as important chemicals or fuel components. However, DDO is challenging due to the high energy barrier needed to break the C-O bond [7,8].

Strong metal–support interactions (SMSI) occur between the reducible metal oxide support and supported transition metal [9–13], which is manifested by the coverage of the transition metal surface by the partially reduced metal oxide after high-temperature hydrogen reduction, resulting in a reduced capacity for CO and H$_2$ chemisorption [14–18]. SMSIs have been extensively investigated, and generally, SMSIs are enhanced with an increase in the reduction temperature. Several works have investigated the effect of SMSIs on the hydrodeoxygenation of phenolic compounds [19–26]. For example, Zhao et al. [21]...
demonstrated that stronger SMSIs of Pt/TiO$_2$ after reduction at 550 °C compared to reduction at 350 °C resulted in an increased turnover frequency (TOF) for the deoxygenation of m-cresol to toluene.

Generally, Ni catalysts show a high C-C hydrogenolysis activity at high temperatures and low pressure, producing large amounts of unfavorable CH$_4$ with high hydrogen consumption [27]. However, at low temperatures and high pressure, Ni catalysts readily hydrogenate the phenyl ring to produce saturated cycloalkanes [28,29]. The properties of metallic Ni can be modified by loading a second metal [30,31], adjusting the Ni particle size [32,33], and combining it with reducible metal oxide as support [34]. In particular, Zhang et al. [35] reported that the large Ni particles on anatase TiO$_2$ are encapsulated by TiO$_x$ after reduction temperatures of > 300 °C and therefore lose activity toward HDO due to the SMSI. In contrast, the highly dispersed Ni atomic clusters inhibit TiO$_x$ encapsulation by interaction with the defective sites of anatase TiO$_2$ and thus improve the selectivity of phenol during HDO of guaiacol. Nevertheless, the authors stated that it could not be excluded that the high selectivity may be attributed to small Ni particles partially covered by TiO$_x$.

Many reports have explored the effect of metal particle size on the HDO of phenolic compounds. On an inert support of SiO$_2$, the change in particle size reflects the nature of a metal. Mortensen et al. [32] found that phenol is readily hydrogenated to cyclohexanol on large Ni particles at 275 °C and 100 bar, while the small Ni particles have a high TOF of deoxygenation to cyclohexane due to more step sites. Our previous HDO work at a low pressure and vapor phase [36] showed that small Ni particles favor deoxygenation of m-cresol to toluene due to more step and corner sites, while large Ni particles favor C-C hydrogenolysis toward CH$_4$ due to more terrace sites. On the other hand, the effect of metal particle size on the HDO activity on a reducible metal oxide support is likely dependent on the synergistic effect of the metal and the support. Mao et al. [37] demonstrated that as the Au particle size is increased from 3 to 41 nm, the conversion of guaiacol decreases from 65 to 36%, resulting from the smaller interfacial area between anatase TiO$_2$ and large Au particles. Similarly, by adjusting the Ru particle size on Ru/TiO$_2$, Otomoso et al. [38] found that the activity of m-cresol deoxygenation to toluene is related to the interfacial perimeter of Ru and TiO$_2$. Despite the fact that it has been reported that the SMSI is more pronounced on larger metal particles [39], metal-particle-size-dependent SMSI have rarely been explored for the HDO of phenolics.

In our recent work [40], we compared the effects of the TiO$_2$ crystalline phase and reduction temperature on the HDO of m-cresol. Anatase TiO$_2$ is more readily reduced, resulting in a higher and thicker TiO$_x$ coverage on the Ni particle and, therefore, a stronger SMSI at temperatures > 350 °C, which, however, led to decreased HDO activity due to excessive SMSIs. Very differently, rutile TiO$_2$ is less reducible. A moderate (optimal) SMSI could only be achieved on Ni/r-TiO$_2$ when the reduction temperature was increased to 650 °C, resulting in the highest activity for HDO. More importantly, the selectivity of direct deoxygenation reached 84.8% at 100% m-cresol conversion. However, the effect of Ni particle size on the SMSI of Ni/TiO$_2$ for HDO was not explored in that study.

In this study, we prepared a series of rutile TiO$_2$-supported Ni catalysts with various Ni sizes by tuning the amount of Ni loadings. The relationship between Ni particle size and the degree of the SMSI was investigated, and the consequences on the HDO of m-cresol were elucidated. The results showed that the SMSI is dependent on the Ni particle size, and the larger the Ni particle size, the stronger the SMSI. The coverage of the Ni surface by TiO$_x$ improves the deoxygenation of m-cresol to toluene while inhibiting C–C hydrogenolysis toward CH$_4$. Moreover, the TOF of HDO on a small Ni size of 4 nm is >2 times higher than that on a large Ni size of 29.1 nm due to the moderate SMSI.
2. Results and Discussion

2.1. Catalyst Characterization

Figure 1 shows the XRD patterns of Ni/TiO₂ catalysts with varying amounts of Ni loadings. Only the rutile phase of TiO₂ is identified for all samples, indicating no TiO₂ phase transition takes place after reduction at 650 °C. No diffractions of Ni species are observed for 1Ni/r-TiO₂, which suggests Ni is highly dispersed, while metallic Ni diffractions at 2θ of 44.41° and 51.85° are observed for 5Ni/r-TiO₂ and 10Ni/r-TiO₂, which correspond to Ni(111) and (200), respectively. It is evident that the diffraction peak of Ni(111) becomes stronger and sharper with increasing Ni loadings (see inset), pointing to the fact that high Ni loading leads to the agglomeration of Ni particles. According to the Scherrer formula, the average Ni particle sizes of 5Ni/r-TiO₂ and 10Ni/r-TiO₂ are estimated to be 17.2 and 23.1 nm, respectively.

![XRD patterns of 650 °C reduced catalysts](image)

Figure 1. XRD patterns of 650 °C reduced (a) 1Ni/r-TiO₂, (b) 5Ni/r-TiO₂, and (c) 10Ni/r-TiO₂.

H₂-TPR is used to probe the interaction between Ni and rutile TiO₂. As shown in Figure 2, the bare rutile TiO₂ consumes few H₂ at high reduction temperatures. A reduction peak at 494 °C is observed for 1Ni/r-TiO₂, which is attributed to the reduction of small Ni particles strongly interacting with r-TiO₂. As the amount of Ni loading is increased, another peak emerges at lower temperatures, which can be ascribed to the reduction of larger Ni particles with weaker interaction with r-TiO₂. This peak increases in intensity and shifts to lower temperatures from 387 to 378 °C with increasing Ni loadings from 5% to 10%, indicating larger NiO particles are present for 10Ni/r-TiO₂. The quantified hydrogen consumption is summarized in Table 1. It is evident that the H₂/Ni molar ratio is higher than 1 for all samples, indicating besides the complete reduction of NiO, the r-TiO₂ support is also partially reduced. This phenomenon is related to the spillover of H from metallic Ni to TiO₂ support, resulting in a partial reduction of TiO₂ in proximity to Ni. It is important to note that the H₂/Ni molar ratio is the highest on 1Ni/r-TiO₂ (1.41) and decreases with increasing Ni loadings, which suggests that a smaller Ni particle favors more H₂ spillover due to high Ni dispersion.

The representative TEM images of 1Ni/r-TiO₂, 5Ni/r-TiO₂, and 10Ni/r-TiO₂ are shown in Figure 3. The number-weighted-average Ni particle size is 4 nm for 1Ni/r-TiO₂ and increases to 23.8 and 29.1 nm for 5Ni/r-TiO₂ and 10Ni/r-TiO₂, respectively (Table 2), which are in good agreement with the XRD results. The Ni dispersion was measured by CO chemisorption. As shown in Table 2, the dispersion of Ni decreases from 1.03 to 0.6% with increasing Ni loadings. It is important to note that the CO chemisorption-measured Ni dispersions are much lower than those estimated from Ni particle size (Table 2). Such a difference points to the occurrence of an SMSI. That is, the spillover H from Ni reduces the adjacent TiO₂, and then the partially reduced TiOₓ (x < 2) migrates onto the surface of the...
Ni particle to form an overlayer, which leads to a decrement in the accessibility of surface Ni by CO.

![Figure 2. H2-TPR profiles for 1Ni/r-TiO2, 5Ni/r-TiO2, 10Ni/r-TiO2, and r-TiO2 catalysts.](image)

**Table 1.** H2 consumption and molar ratio of H2/Ni over 1Ni/r-TiO2, 5Ni/r-TiO2, and 10Ni/r-TiO2 catalysts determined by H2-TPR.

| Sample       | H2 Consumption Total (mmol·g⁻¹) | H2/Ni | Sample Metal Ni (mmol·g⁻¹) a |
|--------------|---------------------------------|-------|-----------------------------|
| 1Ni/r-TiO2   | 0.024                           | 1.41  | 0.017                       |
| 5Ni/r-TiO2   | 0.096                           | 1.14  | 0.084                       |
| 10Ni/r-TiO2  | 0.175                           | 1.05  | 0.166                       |

a H2 consumption for the complete reduction of NiO to Ni according to the theoretical stoichiometric ratio.

![Figure 3. TEM images of 650 °C reduced (A) 1Ni/r-TiO2, (B) 5Ni/r-TiO2, and (C) 10Ni/r-TiO2 catalysts.](image)

**Table 2.** Ni particle size and dispersion of 1Ni/r-TiO2, 5Ni/r-TiO2, and 10Ni/r-TiO2 catalysts.

| Sample       | Metal Ni dₓ,XRD (nm) a | Metal Ni dₓ,TEM (nm) a | Metal Ni Dispersion b (%) | Metal Ni Dispersion c (%) |
|--------------|------------------------|------------------------|---------------------------|---------------------------|
| 1Ni/r-TiO2   | —                      | 4.0                    | 25                        | 1.03                      |
| 5Ni/r-TiO2   | 17.2                   | 23.8                   | 4.3                       | 0.76                      |
| 10Ni/r-TiO2  | 23.1                   | 29.1                   | 3.5                       | 0.60                      |

a Particle size was derived from XRD; b Particle size was measured by counting > 200 Ni particles in the TEM and estimating the Ni dispersion (dispersion = 1.01/dₓ,TEM [41]); c Ni dispersion achieved by CO chemisorption.

High-resolution (HR) TEM observations were used to visualize the degree of SMSI as a function of Ni particle size (Figure 4) since it has been reported that the SMSI is sensitive to the metal particle size [39]. As shown in Figure 4A,B, a small 5 nm Ni particle (dₓ,000 = 0.180 nm) is located on the surface of TiO2 for 1Ni/r-TiO2. Interestingly, this particle...
is partially covered by a thin TiO$_x$ overlayer of ~0.4 nm. The extent of coverage increases and the overlayer becomes thicker with an increase in the Ni particle size. For 5Ni/r-TiO$_2$ (Figure 4C,D), a TiO$_x$ overlayer of ~0.64 nm partially covers a Ni particle (d$_{111}$ = 0.204 nm) of ~10 nm. The TiO$_x$ overlayer thickens further to ~1.37 nm for 10Ni/r-TiO$_2$ and appears to completely encapsulate a Ni particle of ~20 nm (Figure 4E,F).

![HR-TEM images](image)

**Figure 4.** HR-TEM images of 650 °C-reduced (A–B) 1Ni/r-TiO$_2$, (C–D) 5Ni/r-TiO$_2$, and (E–F) 10Ni/r-TiO$_2$. The white line indicates the lattice stripes of Ni(111) and Ni(200), and the purple arrow highlights the TiO$_x$ overlayer and marks its thickness with a green line.

The electronic structure of Ni/r-TiO$_2$ catalysts was explored by XPS. Figure 5 shows the Ni 2p and Ti 2p spectra of Ni/r-TiO$_2$ samples with different Ni loadings. For 1Ni/r-TiO$_2$, the binding energy of Ni$^0$ is at 852.4 eV, while the binding energies of Ni$^{2+}$ and the
saturates of Ni$^{2+}$ are at 856 and 861.7 eV, respectively (Figure 5A). As the samples were reduced ex situ; the Ni surface was partially oxidized when transferring the sample to the XPS chamber. Compared to 1Ni/r-TiO$_2$, the binding energy of Ni$^{0}$ for 5Ni/r-TiO$_2$ and 10Ni/r-TiO$_2$ shifts to lower values by 0.2 eV and 0.4 eV, respectively. One may expect the increased Ni encapsulation by TiO$_x$ with increasing Ni loadings (see Figure 4) results in more electron transfer from oxygen vacancies (O$_v$-Ti$^{3+}$) to Ni, producing electron-rich Ni$^{0}$. In addition, the Ni$^{0}$/Ni$^{2+}$ ratio rises from 0.09 to 0.22 with an increase in Ni loading (Table 3). This likely resulted from stronger SMSIs, i.e., more encapsulation of Ni by TiO$_x$ for the 10Ni/r-TiO$_2$ sample, which prevented the oxidation of surface Ni during exposure to air. On the other hand, the peak of Ti$^{3+}$ is tiny relative to that of Ti$^{4+}$ for all samples (Figure 5B), reflecting that rutile TiO$_2$ is difficult to be reduced. Additionally, the Ti$^{3+}$/Ti$^{4+}$ ratio increases with increasing Ni loadings (Table 3), which indicates more of the Ti species was reduced at higher Ni loadings.

![Figure 5. (A) Ni 2p and (B) Ti 2p XPS spectra of 650 °C-reduced 1Ni/r-TiO$_2$, 5Ni/r-TiO$_2$, and 10Ni/r-TiO$_2$.](image)

| Sample          | Ni$^{0}$/Ni$^{2+}$ | Ti$^{3+}$/Ti$^{4+}$ |
|-----------------|-------------------|---------------------|
| 1Ni/r-TiO$_2$   | 0.09              | 0.03                |
| 5Ni/r-TiO$_2$   | 0.17              | 0.04                |
| 10Ni/r-TiO$_2$  | 0.22              | 0.06                |

2.2. Catalytic Performance

The activities of bare supports (SiO$_2$ and r-TiO$_2$) and supported Ni catalysts (1Ni/SiO$_2$ and 1Ni/r-TiO$_2$) in the HDO of m-cresol were compared at 350 °C and W/F of 2 h. As shown in Figure 6, the bare supports are inactive for HDO m-cresol (conversion < 1%), while the supported Ni catalysts are active for the HDO reaction. The type of support plays a crucial role in the major product distributions. The major product over 1Ni/SiO$_2$ is phenol (Ph). CH$_4$ and deoxygenation products of benzene (Ben) and toluene (Tol) are the minor products. Consistent with previous work [27], the results indicate that the metallic Ni favors the C-C hydrogenolysis reaction over the deoxygenation reaction under the current reaction condition. In contrast to 1Ni/SiO$_2$, although the conversion is slightly lower, Tol and dimethylbiphenyl (DMB) are the major products on 1Ni/r-TiO$_2$. More importantly, almost no CH$_4$ is formed. This result highlights that the combination of reducible r-TiO$_2$ and Ni provides a unique catalytic activity for the direct deoxygenation of m-cresol to Tol. The TiO$_x$ overlayer on the Ni surface inhibits the C-C hydrogenolysis activity on the metallic Ni, and the Ni-TiO$_x$ interfacial site enhances the deoxygenation activity.
m-Cresol conversion and major product yields and on bare supports (SiO$_2$ [31] and r-TiO$_2$) and supported Ni catalysts (1Ni/SiO$_2$ and 1Ni/r-TiO$_2$). Reaction conditions: T = 350 °C, P = 1 atm, H$_2$ / m-cresol = 50, TOS = 30 min, W/F = 2 h. Product with a yield of less than 0.2% is not listed. Ben, Tol, Iso-Cr, Ph, DMB, and C$_{14}$O represent benzene, toluene, cresol isomers, phenol, dimethylbiphenyl, and 5,5’-dimethyl-3-hydroxybiphenyl, respectively.

The effect of Ni loadings on Ni/r-TiO$_2$ was then investigated for m-cresol HDO at 350 °C and W/F of 2 h. As the Ni loading is increased from 1% to 10%, m-cresol conversion increases from 20.3% to 54.5% (Figure 7). The Tol yield and the total aromatics yield (Ben, Tol, and DMB) follow the same trend. Previous work of HDO on Ni/SiO$_2$ under similar reaction conditions showed that when the Ni particle size increases from 2 to 22 nm, the selectivity toward C-C hydrogenolysis increases while selectivity toward deoxygenation decreases [36]. In the present work, almost no CH$_4$ is produced on 10Ni/r-TiO$_2$ despite the Ni particle size being as large as 29.1 nm. This difference suggests that Ni particle size on Ni/r-TiO$_2$ is not the dominant factor that determines product distribution. In contrast, the SMSI appears to be the key to tune the reaction pathway from hydrogenolysis to direct deoxygenation.

To further compare the effect of Ni particle size, the conversion of m-cresol and the evolution of major product yields as a function of W/F were studied. As illustrated in Figure 8, Tol is always the dominant product at all conversion levels, irrespective of different Ni particle sizes. In addition, the yield of CH$_4$ is near zero. This result indicates that SMSI changes the properties of the Ni surface. That is, the TiO$_x$ overlayer inhibits the C–C hydrogenolysis activity and increases the deoxygenation activity at the interfacial of Ni–TiO$_x$. The yield of DMB decreases while the yield of xylenols increases with an increase in Ni particle size from 1Ni/r-TiO$_2$ to 10Ni/r-TiO$_2$ (Figure 8B–D). The formation of DMB is completed through the hydrogenation of m-cresol on Ni to methylcyclohexanone (MCHone) and methylcyclohexanol (MCHol), which condense to 5,5’-dimethyl-3-hydroxybiphenyl (C$_{14}$O) on the acid site and then subsequently deoxygenate to DMB (see Figure 9). The xylenols/phenol and cresol isomers (Iso-Cr) are formed through the disproportionation and isomerization of m-cresol on the acidic site [42], respectively (see Figure 9). The trend of increased xylenols at the expense of DMB with an increase in Ni size likely resulted from stronger acid sites of Ti$^{3+}$ [43] being produced on the catalysts with higher Ni loadings.
Figure 7. m-Cresol conversion and major product yields with varying Ni loadings on r-TiO₂. Reaction conditions: T = 350 °C, P = 1 atm, H₂/m-cresol = 50, TOS = 30 min, W/F=2 h. Product with a yield of less than 0.2% is not listed. Ben, Tol, Ph, DMB, and C₁₄O represent benzene, toluene, phenol, dimethylbiphenyl, and 5,5'-dimethyl-3-hydroxybiphenyl, respectively.

Table 4 compares the selectivity of the products at the near-complete conversion of m-cresol on three catalysts. The selectivity of aromatics (Tol, Ben, Xylene, and DMB) decreases slightly from 95.4% for 1Ni/r-TiO₂ to 92.9% for 5Ni/r-TiO₂ and then decreases significantly to 83.2% for 10Ni/r-TiO₂. The total selectivity of the products generated on the acidic sites (C₁₄O, Ph, Xylenol, and Iso-Cr) shows an opposing trend. That is, the selectivity increases from 4.4% on 1Ni/r-TiO₂ to 14.7% on 10Ni/r-TiO₂. This trend likely reflects that more Ti³⁺ cations are formed by spillover H from Ni at high Ni loadings.
**Figure 9.** Proposed major reaction pathway during hydrodeoxygenation on Ni/r-TiO$_2$ catalysts.

**Table 4.** Product yields at near-complete conversion of m-cresol over 1Ni/r-TiO$_2$, 5Ni/r-TiO$_2$, and 10Ni/r-TiO$_2$.

| Catalyst   | 1Ni/r-TiO$_2$ | 5Ni/r-TiO$_2$ | 10Ni/r-TiO$_2$ |
|------------|---------------|---------------|---------------|
| W/F        | 6             | 4             | 3             |
| Conversion(%) | 97.75         | 99.25         | 95.2          |
| Selectivity(%) |               |               |               |
| Tol        | 78.37         | 85.41         | 71.46         |
| DMB        | 16.89         | 6.47          | 8.32          |
| Ben        | 0.13          | 1.01          | 3.37          |
| Xylene     | 0             | 0.05          | 0             |
| C$_{14}$O  | 2.20          | 1.58          | 4.60          |
| Ph         | 0.07          | 0.26          | 1.30          |
| Xylenol    | 2.05          | 3.63          | 8.63          |
| Iso-Cr     | 0.04          | 0.01          | 0.19          |
| MCHone     | 0             | 0             | 0             |
| MCHol      | 0.04          | 0             | 0             |
| C$_2$-C$_6$| 0.02          | 0.07          | 0.27          |
| CH$_4$     | 0.02          | 0.23          | 1.01          |

Reaction conditions: T = 350 $^\circ$C, P = 1 atm, H$_2$/m-cresol = 50, TOS = 30 min, W/F was adjusted to obtain a similar conversion of m-cresol.

The intrinsic m-cresol conversion rates, Tol, and total aromatic formation rates were measured at conversions < 10%. As reported in Table 5, the conversion and Tol formation rates increase significantly from 9.66 and 6.33 $\mu$mol·g$^{-1}$·min$^{-1}$ for 1Ni/r-TiO$_2$ to 23.45 and 15.69 $\mu$mol·g$^{-1}$·min$^{-1}$ for 5Ni/r-TiO$_2$, respectively. However, these rates increase only slightly when the Ni loading is further increased by 10%. In contrast, a reverse trend is found for the TOF, which is estimated using the Ni dispersion measured by CO chemisorption. The TOFs of both m-cresol conversion and Tol formation are the highest on 1Ni/r-TiO$_2$ with a small Ni size of 4 nm, and these values decrease gradually with increasing Ni loadings (or Ni particle size). Specifically, the TOFs on 1Ni/r-TiO$_2$ (Ni size of 4 nm) are > 2 times higher than those on 10Ni/r-TiO$_2$ (Ni size of 29.1 nm). These results indicate that a small Ni size with a moderate extent of SMSI is more active for the deoxygenation of m-cresol. On the one hand, the small Ni particle itself is more active in the HDO reaction [36,38]. On the other hand, too strong of an SMSI encapsulates the Ni particle too much and therefore modifies the property of Ni. Consequently, the hydrogenation ability of Ni may be lowered, which eventually lowers the TOF.
found for the TOF, which is estimated using the Ni dispersion measured by CO chemi-

| Sample     | Reaction Rate (µmol·g⁻¹·min⁻¹)  | Turnover Frequency (min⁻¹) |
|------------|---------------------------------|---------------------------|
|            | m-cresol | Tol | Deoxygenation | m-cresol | Tol | Deoxygenation |
| 1Ni/r-TiO₂ | 9.66     | 6.33 | 7.25 | 5.55 | 3.64 | 4.16 |
| 5Ni/r-TiO₂ | 23.45    | 15.69 | 17.26 | 3.64 | 2.43 | 2.68 |
| 10Ni/r-TiO₂| 25.39    | 15.83 | 17.95 | 2.48 | 1.54 | 1.75 |

a Measured at conversion < 10%. Reaction conditions: T = 350 °C, P = 1 atm, H₂/m-cresol = 50, TOS = 30 min;

b Deoxygenation represents aromatics products (benzene, toluene, and DMB).

Table 5. The intrinsic reaction rate and turnover frequency (TOF) for HDO of m-cresol.

At a high reduction temperature of 650 °C, Ni is partially covered by reduced TiOₓ, forming the Ni-TiOₓ interfacial sites. Compared with Ni/SiO₂, the TiOₓ overlayer on Ni/r-TiO₂ improves the direct deoxygenation activity, making Tol the major product. This can be explained by the adsorption of oxygen atoms of m-cresol at oxygen vacancies and the adsorption of a phenyl ring on Ni, which facilitates the C-O breakage [44]. In addition, the degree of SMSI is closely related to the Ni particle size. The thickness of the TiOₓ overlayer and its coverages on the Ni surface increase as the Ni particle size is increased (Figure 4). Too much coverage of TiOₓ on large Ni particles at high loadings reduces the surface Ni that is accessible by m-cresol, which eventually reduces the activity in HDO. As the Ni loading increases, more TiOₓ is reduced (see XPS results), resulting in increased acid-catalyzed reactions, such as disproportionation. In summary, a small Ni particle with moderate SMSI appears to be optimal for the direct deoxygenation of m-cresol to toluene.

As shown in Figure 10, the three catalysts showed a similar deactivation trend with time on stream. The conversion decreased rapidly in the first 2 h, and then the deactivation became very slow. It is important to note that Tol is always the dominant product, which likely indicates the deactivation is due to the loss of the number of active sites.

![Figure 10. Cont.](image-url)
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Figure 10. Stability of (A) 1Ni/r-TiO2-H650, (B) 5Ni/r-TiO2-H650, and (C) 10Ni/r-TiO2-H650 catalysts during HDO of m-cresol. Reaction conditions: T = 350 °C, P = 1 atm, H2/m-cresol = 50. W/F in the figure are: (A) 5 h, (B) 3 h, and (C) 2.7 h, respectively. Ben, Tol, MCHone, MCHol, Iso-Cr, Ph, DMB, and C14O represent benzene, toluene, methylcyclohexanone, methylcyclohexanol, cresol isomers, phenol, dimethylbiphenyl, and 5,5′-dimethyl-3-hydroxybiphenyl, respectively.

3. Experimental

3.1. Catalyst Preparation

Catalysts with varying amounts of Ni loadings were prepared using an incipient wetness impregnation method. Rutile TiO2 (r-TiO2, 99.8%, 13.9 m²/g Macklin, Shanghai, China) was added to a Ni(NO3)2·6H2O (Aladdin, Shanghai, China, 98%) precursor solution, after which the samples were aged at room temperature for 12 h and dried at 100 °C for 12 h. All catalysts were calcined at 400 °C for 4 h at a ramping rate of 2 °C/min. The catalysts were named xNi/r-TiO2, where x (x = 1, 5, and 10) is the mass fraction (%) of Ni in the catalysts.

3.2. Catalyst Characterization

X-ray diffraction (XRD) was measured on a Rigaku D/max 2500 (JEOL, Tokyo, Japan) diffractometer using Cu Kα as the radiation source. The 2θ angle range of the scan is 20–80°, and the scanning rate is 6°/min. The transmission electron microscopy (TEM) observation
of the samples was performed in a JEM-F200 electron microscope (JEOL, Tokyo, Japan) at 200 KV. Approximately 200 particles were analyzed to calculate the average particle size of Ni. Hydrogen temperature-programmed reduction (H\textsubscript{2}-TPR) of the catalysts was measured on a Chemisorb 2750 (Micrometrics, Atlanta, GA, USA). A catalyst sample of 100 mg was charged in a U-shaped quartz tube, pretreated by purging in flowing N\textsubscript{2} for 1 h at 300 °C, and was finally cooled to room temperature. The sample was heated from room temperature to 800 °C in 10% H\textsubscript{2}/Ar at a rate of 10 °C/min. The consumption of H\textsubscript{2} during TPR was monitored via a TCD detector. The amount of H\textsubscript{2} consumed was calibrated by a reduction of a known amount of CuO. The stoichiometric H\textsubscript{2}/NiO ratio was assumed as 1 to estimate the theoretical H\textsubscript{2} needed for complete reduction of NiO. The CO chemisorption was measured in the same equipment used for H\textsubscript{2}-TPR. The catalyst was reduced at 650 °C for 1 h, followed by purging by flowing He for 30 min and finally cooling to room temperature. After the baseline was stabilized, pulses of 5% CO/He (500 µL) were sent onto the sample until a constant CO peak was achieved. The stoichiometric CO/Ni ratio was assumed as 1 to estimate the dispersion of Ni. The X-ray photoelectron spectra (XPS) of the samples were recorded on a PHI 1600 ESCA spectrometer (Chanhassen, MN, USA) fitted with an Al K\textsubscript{α} (1486.6 eV) radiation source and were calibrated with the C1s peak at 284.8 eV.

3.3. Catalytic Activity Measurement

The vapor-phase HDO of m-cresol was performed in fixed-bed reactor at 350 °C and atmospheric pressure. Prior to reaction, the catalyst was reduced in situ with flowing hydrogen (28 mL/min) at 650 °C for 1 h since previous work showed that this reduction condition resulted in optimal SMSI for rutile support. m-Cresol was injected into the reactor by a syringe pump (KDS100, KD scientific). The reactant was vaporized at the injection port before entering the reactor. The molar ratio of H\textsubscript{2}/m-cresol was maintained at 50 for all runs. The products were quantified online using a gas chromatograph (GC, 7890B, Agilent, Santa Clara, CA, USA). All lines were wrapped with heating tape and kept at 230°C to ensure no condensation. Space time (W/F, h) was defined as the ratio of weight of catalyst (g) to the organic feed flow rate (g/h).

4. Conclusions

We prepared a series of Ni/r-TiO\textsubscript{2} catalysts with different Ni particle sizes by varying the amount of Ni loadings. These catalysts were reduced at 650 °C and tested at 350 °C and atmospheric pressure for hydrodeoxygenation of m-cresol. The particle size dependence of SMSI was observed. A small Ni size of 4 nm resulted in a thin and partial TiO\textsubscript{x} coverage; however, a large Ni particle of 29.1 nm led to a thick and almost complete TiO\textsubscript{x} coverage. The SMSI inhibited the C-C hydrogenolysis reaction of Ni while promoting the direct deoxygenation activity at the Ni-TiO\textsubscript{x} interfacial site. The TOF of deoxygenation to toluene on 1Ni/r-TiO\textsubscript{2} with 4 nm Ni is > 2 times higher than that on 10Ni/r-TiO\textsubscript{2} with 29.1 nm Ni. This result indicates that a small Ni particle with a moderate SMSI appears to be optimal for the direct deoxygenation of m-cresol to toluene.

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