

## Article

# Novel Fe-W-Ce Mixed Oxide for the Selective Catalytic Reduction of NO<sub>x</sub> with NH<sub>3</sub> at Low Temperatures

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**Abstract:** A set of novel iron doped cerium-tungsten catalysts were prepared by sol-gel method with a view to their application for low temperature selective catalytic reduction (SCR) of NO<sub>x</sub> with NH<sub>3</sub> in power plants. With a molar ratio Fe/W/Ce of 0.5:1:1, a NO<sub>x</sub> reduction of >90% at 200 °C was achieved. In Fe-W-Ce catalysts with low iron oxide content, it was found that the iron compounds were highly dispersed and formed a solid solution within the cerium oxide lattice, which promoted the SCR activity. Large amounts of iron in the catalysts might form a layer of Fe<sub>2</sub>O<sub>3</sub> on the catalyst surface, which induced the synergistic inhibition effect among Fe, Ce and W species. Moreover, the Fe-W-Ce catalysts possessed a high resistance to changed operation parameters as well as to deactivation by SO<sub>2</sub> and/or H<sub>2</sub>O. The novel catalyst showed to be competitive among recently developed low-temperature SCR catalysts.

**Keywords:** Fe-W-Ce; SCR; synergistic effect; high resistance; competitive

## 1. Introduction

During combustion processes, many different kinds of pollutants can be generated, such as NO<sub>x</sub>. NO<sub>x</sub> emissions can have a strong negative impact on the environment and on human health, which result in photochemical smog and acid rain [1]. To avoid these damages, several techniques for the abatement of NO<sub>x</sub> (DeNO<sub>x</sub>) have been developed in the past. A widely applied technique of NO<sub>x</sub> abatement is the selective catalytic reduction (SCR) with ammonia (NH<sub>3</sub>) as reduction agent. Mostly vanadium catalysts on titanium support doped with tungsten or molybdenum oxide are commercially used (denoted as V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub>/TiO<sub>2</sub>, respectively) in a relatively narrow temperature window of 300–400 °C [2,3]. However this system has some problems, such as the volatility and toxicity of vanadium species, poisoning by K<sub>2</sub>O and PbO, low N<sub>2</sub> selectivity at high temperatures and high conversion of SO<sub>2</sub> to SO<sub>3</sub> [4]. Therefore, it is necessary to develop novel catalysts that operate at lower temperatures [5].

With the aim to find a replacement for conventional catalysts, diverse catalysts have been studied extensively over the past years, such as Mn-oxides [6] and other transition metals oxides such as Ce-Fe/TiO<sub>2</sub> [7], CuO/Ti<sub>0.95</sub>Ce<sub>0.05</sub>O<sub>2</sub> [8], Ce-Nb binary oxide [9], Ba/CeO<sub>2</sub>-MO<sub>x</sub> (M = Mn, Fe) mixed oxides [10], Ce-Sn-O<sub>x</sub> [11] or Ce-Ta mixed oxides [12] have been used as additives. Iron oxide is

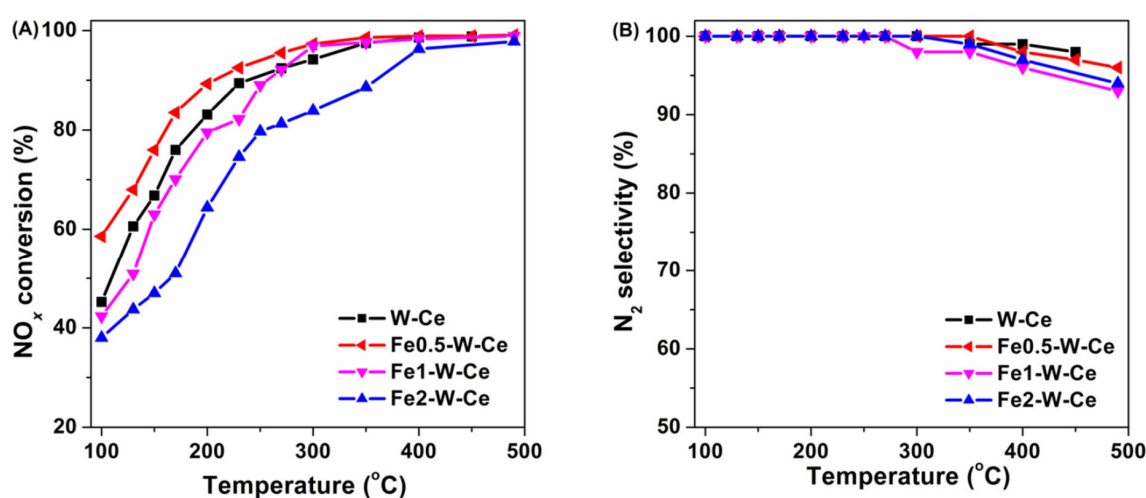
reported to especially enhance the  $\text{NO}_x$  conversion at low temperatures. Moreover, Fe-doped Mn-Ce/TiO<sub>2</sub> catalysts can be used since iron is said to enhance the resistance to H<sub>2</sub>O and SO<sub>2</sub> [13,14]. Additionally, the shift between Ce<sup>3+</sup> and Ce<sup>4+</sup> is also hold responsible for the enhancement of NO to NO<sub>2</sub> oxidation by cerium oxide, which favors the fast SCR reaction [15,16]. In addition, tungsten oxide is reported to widen the operation temperature window. For example, Shan et al. describe a NO<sub>x</sub> conversion of almost 100% from 250 to 450 °C over Ce-W mixed oxides [17,18]. The WO<sub>3</sub>-ZrO<sub>2</sub> catalyst exhibited >80% NO<sub>x</sub> conversion at temperatures as low as 150 °C [19]. A reason may be that WO<sub>3</sub> is said to increase the strength and amount of Brönsted acid sites on catalyst surface [20]. Chen et al. assume that tungsten promotes the NO to NO<sub>2</sub> oxidation, which facilitates the fast SCR reaction that can occur at low temperatures [21]. Furthermore, tungsten seems to have the ability to inhibit the oxidation of NH<sub>3</sub> to N<sub>2</sub>O and therefore increases the N<sub>2</sub> selectivity [19]. Besides, in combination with Ce, tungsten addition can lead to an improved dispersion of Ce and the amount of Ce<sup>3+</sup> which leads to an increased chemisorption of oxygen [20].

Thus the combination of cerium and tungsten with iron might promise a high NO<sub>x</sub> reduction ability at lower temperatures with a high N<sub>2</sub> selectivity and good resistance to deactivation by diverse compounds. This novel catalyst is developed and characterized, and the catalytic performance is also tested under diverse conditions, such as varying gas hourly space velocities (GHSV), SO<sub>2</sub> and H<sub>2</sub>O flue gas content and NH<sub>3</sub>/NO ratio. The results of these tests shall facilitate an estimation of the catalyst's behavior under "real" conditions in a power plant.

## 2. Results

### 2.1. Activity Measurement

Figure 1 shows the NH<sub>3</sub>-SCR performance for all tested catalysts over a temperature range of 100 to 500 °C. Without Fe doping, the W-Ce catalyst showed more than 80% NO<sub>x</sub> conversion at above 190 °C. The addition of Fe to W-Ce mixed oxide has obvious influence on the catalytic activity. When the Fe/W/Ce molar ratio was controlled at 0.5:1:1, the low temperature SCR activity was significantly enhanced with 80% NO<sub>x</sub> conversion at 160 °C. Further increasing the Fe/W/Ce molar ratio to 1:1:1 and 2:1:1 resulted in the lower SCR activity, and the 80% NO<sub>x</sub> conversion could be obtained at as high as 250 °C. Moreover, all catalysts also showed the higher N<sub>2</sub> selectivity (>95%) in the whole temperature range (Figure 1B). Therefore, the optimal Fe addition could contribute to improving the NH<sub>3</sub>-SCR activity.



**Figure 1.** (A) NO<sub>x</sub> conversion; and (B) N<sub>2</sub> selectivity of Fe-W-Ce catalysts. Reaction conditions: [NO<sub>x</sub>] = 450 ppm, [NH<sub>3</sub>] = 450 ppm, 2.5% O<sub>2</sub>, N<sub>2</sub> as balance, GHSV = 20,000 h<sup>-1</sup>.

## 2.2. BET and XRD

All the samples show type IV isotherms according to the International Union of Pure and Applied Chemistry (IUPAC) classification (shown in Figure S1), which are typical for mesoporous materials (pore diameter 2–50 nm) [8]. The results of the BET analysis for this study are listed in Table 1. It could be found that compared to W-Ce catalyst, the specific surface area was almost tripled at the highest iron loading. This also indicated that there was no link between a large specific surface area and a good catalytic performance. In addition, the molar ratio of Fe/W/Ce in samples (determined by inductively coupled plasma and atomic emission spectrometry (ICP-AES), Table 1) is more or less the same to the theoretical value. The XRD patterns of the Fe containing catalysts are compared to the W-Ce catalyst in Figure 2. All peaks of W-Ce catalyst can be assigned to cerianite ( $\text{CeO}_2$ ,  $2\theta = 28.7^\circ, 33.8^\circ, 47.4^\circ, 56.0^\circ, 69.5^\circ$  and  $76.6^\circ$ ) and tungsten oxide ( $\text{WO}_3$ ,  $2\theta = 23.7^\circ, 28.7^\circ, 33.8^\circ, 41.6^\circ, 47.4^\circ, 49.9^\circ, 53.8^\circ$  and  $60.2^\circ$ ). This accorded with other studies in which  $\text{CeO}_2$  and  $\text{WO}_3$  were also the dominant species [21]. Meanwhile, the peaks were not very sharp, which pointed at low crystallinity of the sample [16]. This phenomenon might result from the addition of  $\text{WO}_3$  to  $\text{CeO}_2$  as reported in literature, which was regarded to be an indication of strong interactions between the metal oxides [22]. For Fe0.5-W-Ce catalyst, no new peaks appear, but the  $\text{CeO}_2$  and  $\text{WO}_3$  peaks became less intense and broader. This was reflected by the small crystallite size of the sample, which was usually associated with a high catalytic performance [22]. In addition, two possible explanations were given for the absence of new peaks from Fe compounds in Fe0.5-W-Ce. First, Fe oxides existed in an amorphous state and were highly dispersed over the surface of the  $\text{WO}_3$  and  $\text{CeO}_2$  lattice [14]. Second, smaller Fe ions (atomic radius 140 pm) can substitute larger Ce ions (atomic radius 185 pm) in the  $\text{CeO}_2$  lattice [23], Fe/Ti oxides [24] as well as Fe/Mn oxides [25].

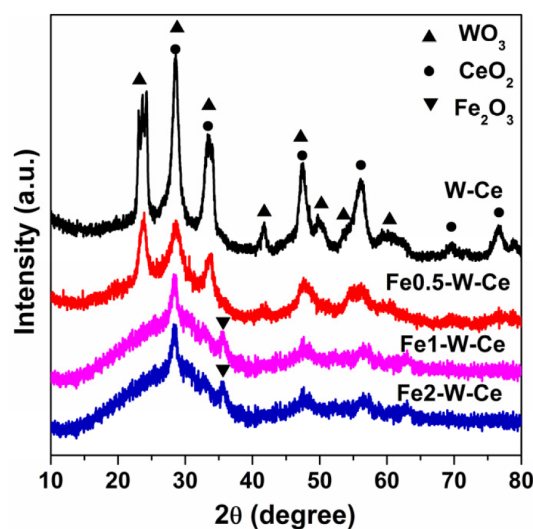


Figure 2. XRD patterns of Fe-W-Ce catalysts.

Table 1. Specific surface area and crystallite of different catalysts.

| Samples    | BET Surface Area ( $\text{m}^2/\text{g}$ ) | Crystallite Size (nm) | Fe/W/Ce Molar Ratio <sup>a</sup> |
|------------|--|-----------------------|----------------------------------|
| W-Ce       | 24.8                                       | 10.5                  | 1.09:0.96                        |
| Fe0.5-W-Ce | 39.4                                       | 5.4                   | 0.61:1.03:1.06                   |
| Fe1-W-Ce   | 53.2                                       | 7.3                   | 1.08:0.95:1.03                   |
| Fe2-W-Ce   | 77.0                                       | 12.8                  | 2.12:1.03:1.10                   |

<sup>a</sup> Detected by ICP-AES.

For Fe1-W-Ce and Fe2-W-Ce catalysts, the larger crystallite size was observed compared with W-Ce and Fe0.5-W-Ce samples (Table 1). Nevertheless the peak at  $35^\circ$  allowed a clear identification as  $\gamma\text{-Fe}_2\text{O}_3$ , which has previously been reported to form in Fe catalysts [13]. Probably, the appearance of the peak meant that the Fe ions can no longer be incorporated into the Ce lattice. Instead, a layer

of  $\text{Fe}_2\text{O}_3$  formed on the catalyst surface. This phenomenon already occurred for other catalysts with high iron loadings [26]. It might be concluded that this  $\text{Fe}_2\text{O}_3$  layer covered the catalyst surface and hindered the interaction between the W-Ce, which induced the lower  $\text{NH}_3$ -SCR activity.

### 2.3. Raman Characterization

Figure 3 depicts the Raman spectrum of the samples investigated in this work. The spectrum of W-Ce shows a sharp peak at  $460\text{ cm}^{-1}$ , which belongs to the  $\text{F}_{2g}$  mode of the symmetric breathing mode of oxygen atoms surrounding cerium ions in the cubic fluorite phase  $\text{CeO}_2$  [27]. In addition, typical  $\text{WO}_3$  crystallization peaks ( $272$ ,  $711$  and  $810\text{ cm}^{-1}$ ) occur on the W-Ce catalysts, which agrees with the XRD results. However, it is worth mentioning that the peak that belonged to the  $\text{CeO}_2$  becomes weaker significantly for Fe0.5-W-Ce catalyst, which may be related with the decreased  $\text{CeO}_2$  particle size (Table 1) [28]. As for Fe1-W-Ce and Fe2-W-Ce catalyst, the spectrum of  $\text{CeO}_2$  becomes stronger than that of Fe0.5-W-Ce, suggesting that only proper adding of Fe inhibited the crystallization of  $\text{CeO}_2$ . The conclusion is highly consistent with the XRD results.

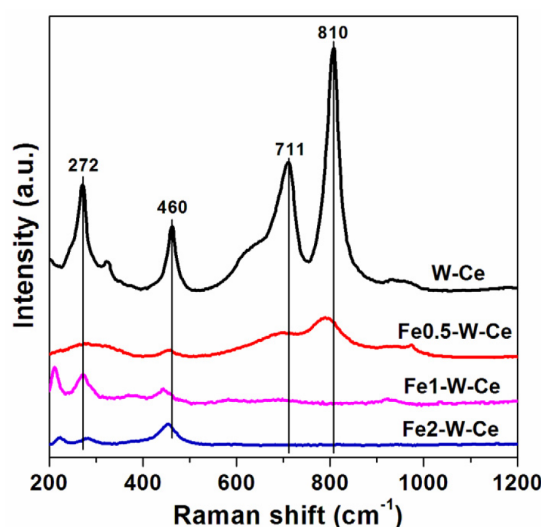


Figure 3. Raman patterns of Fe-W-Ce catalysts.

### 2.4. UV-Vis Diffuse Reflectance Spectroscopy

Figure 4 shows the UV-vis absorption spectra of W-Ce, Fe0.5-W-Ce, Fe1-W-Ce and Fe2-W-Ce. All samples contain three absorption maxima centered at  $\sim 230\text{ nm}$ ,  $290\text{ nm}$  and  $320\text{ nm}$ . The former maxima corresponded to  $\text{Ce}^{3+} \rightarrow \text{O}^{2-}$  charge transfer transitions [29], which implied the occurrence of oxygen vacancy defects [30]. The latter two adsorption maxima were ascribed to oxygen-to- $\text{Ce}^{4+}$  charge transfer and interband transitions, respectively [31]. In addition, an additional peak shoulder can be identified around  $380\text{ nm}$ , which is attributed to  $\text{WO}_3$  [32]. An obvious blue shift of the peaks corresponding to tungsten and ceria compounds can be seen compared with pure  $\text{WO}_3$ . This may be a result of a strong interaction between tungsten and ceria species [33]. These findings are in accordance with the XRD results, which predicted also strong interaction between ceria and tungsten.

Meanwhile, Fe compounds show a broad peak centered at  $530\text{ nm}$ . In literature the peak has been assigned to large  $\text{Fe}_2\text{O}_3$  particles [34]. The intensity of the peaks can be correlated with the degree of dispersion of metal oxides. The Fe1-W-Ce catalyst shows a higher intensity peak of  $\text{Fe}_2\text{O}_3$ , suggesting that a relatively lower dispersion of  $\text{Fe}_2\text{O}_3$  in Fe1-W-Ce catalyst. The peak intensity of Fe2-W-Ce is higher than Fe1-W-Ce, which approves that Fe2-W-Ce shows the lowest dispersion of  $\text{Fe}_2\text{O}_3$ . The results confirm that the Fe compounds in Fe0.5-W-Ce are highly dispersed [24]. Overall, the UV-vis results are in full agreement with the conclusions drawn from the XRD. This includes the strong interaction between  $\text{CeO}_2$  and  $\text{WO}_3$ , the high degree of iron dispersion in Fe0.5-W-Ce and the occurrence of large amounts of  $\text{Fe}_2\text{O}_3$  in the Fe1-W-Ce and Fe2-W-Ce catalyst.

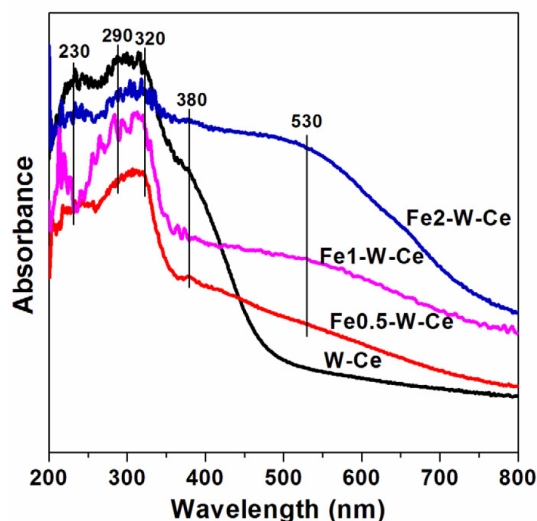


Figure 4. UV-vis of different catalysts.

### 2.5. Influence of GHSV and $\text{NH}_3/\text{NO}$ Ratio

The  $\text{NO}_x$  reduction with different  $\text{NH}_3/\text{NO}$  ratios is shown in Figure 5. Previous experiments have been carried out with a  $\text{NH}_3/\text{NO}$  ratio of 1.2:1. The plot shows that there is a significant decrease of the overall  $\text{NO}_x$  reduction with a  $\text{NH}_3/\text{NO}$  ratio of 0.9:1. A maximal  $\text{NO}_x$  conversion of 91% is reached at 350 °C. Furthermore, the  $\text{NO}_x$  conversion decreases at temperatures >400 °C on  $\text{NH}_3/\text{NO}$  ratio of 0.9:1. This is not observed with higher  $\text{NH}_3/\text{NO}$  ratios. The  $\text{NH}_3/\text{NO}$  ratio has a strong influence on the  $\text{NO}_x$  conversion when it drops below the stoichiometric value of 1. In literature the SCR reaction is described to proceed with zero order concerning  $\text{NH}_3$  at  $\text{NH}_3/\text{NO} > 1$  and with first order for  $\text{NH}_3/\text{NO} < 1$  [35]. This fits with the results shown in Figure 5. For  $\text{NH}_3/\text{NO} > 1$  the adsorption process of  $\text{NH}_3$  to the catalyst surface is said to limit the reaction progress [36]. This is reflected by the minimal difference of the results for  $\text{NH}_3/\text{NO}$  1.1 and 1.2. The strong dependence is not seen as an obstacle for practical application, since the  $\text{NH}_3/\text{NO}$  ratio can be adapted while the process is running.

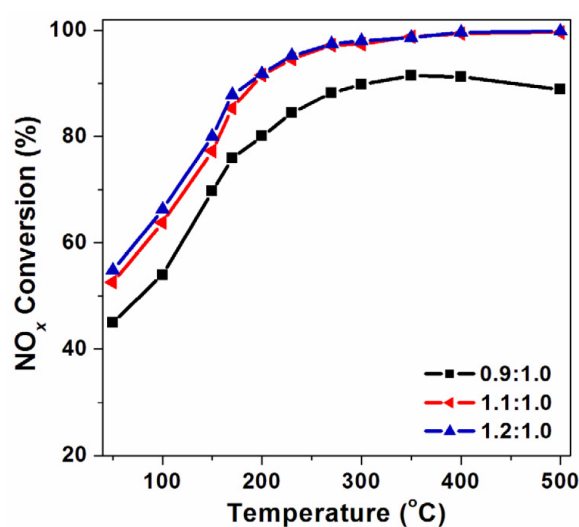
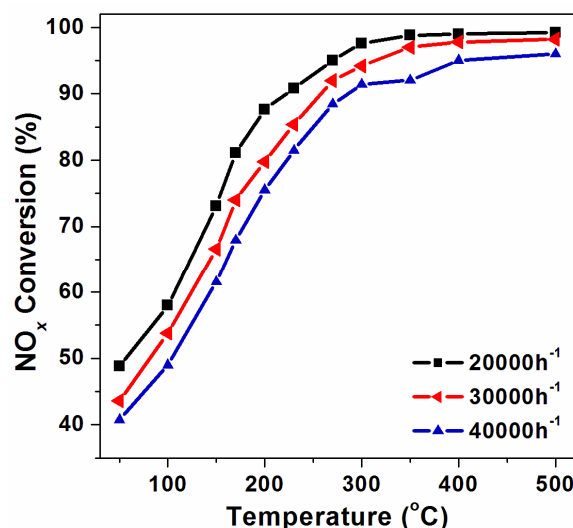


Figure 5. Influence of different  $\text{NH}_3/\text{NO}$  ratios on  $\text{NO}_x$  conversion over Fe0.5-W-Ce catalyst. Reaction conditions:  $[\text{NH}_3] = 450$  ppm, 2.5%  $\text{O}_2$ ,  $\text{N}_2$  as balance, GHSV = 20,000  $\text{h}^{-1}$ .

The influence of GHSV on  $\text{NO}_x$  reduction is tested. Figure 6 shows the slight decrease of  $\text{NO}_x$  conversion from 99% to 96% at 500 °C, when the GHSV is doubled from 20,000 to 40,000  $\text{h}^{-1}$ . The

GHSV has a less pronounced influence on the  $\text{NO}_x$  conversion compared to the  $\text{NH}_3/\text{NO}$  ratio. A variation of the GHSV of 50% (20,000 to 40,000  $\text{h}^{-1}$ ) leads to a  $\text{NO}_x$  conversion of 96%, while a change of the  $\text{NH}_3/\text{NO}$  ratio by only 25% (1.2 to 0.9) decreases the  $\text{NO}_x$  conversion to 91%. Hence, the SCR reaction is more sensitive to changes in the  $\text{NH}_3/\text{NO}$  ratio.

From Figure 6, it can be seen that the impact of GHSV also depends on the reaction temperature. At 500 °C the difference between the  $\text{NO}_x$  conversion with high and low GHSV is only 3.2%, while at lower temperatures, e.g., 170 °C, the difference is 13.1%. This connection was also found by other researchers [37]. The temperature dependence is problematic as far as the practical application is concerned, since it is intended to use the catalysts for low-temperature SCR.



**Figure 6.** Influence of GHSV variation on  $\text{NO}_x$  conversion over Fe0.5-W-Ce catalyst. Reaction conditions:  $[\text{NO}_x] = 450 \text{ ppm}$ ,  $[\text{NH}_3] = 450 \text{ ppm}$ , 2.5%  $\text{O}_2$ ,  $\text{N}_2$  as balance.

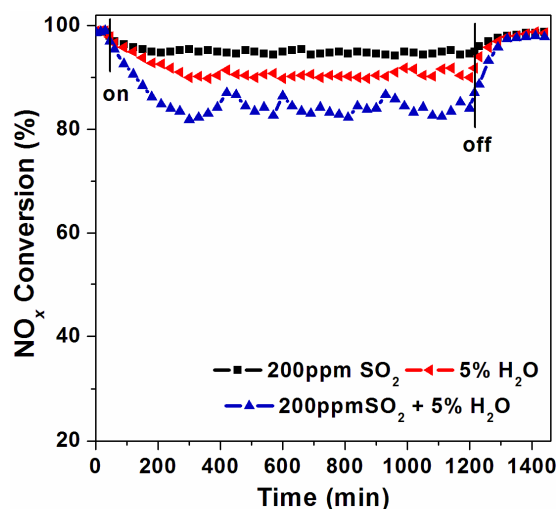
## 2.6. Influence of $\text{SO}_2$ and $\text{H}_2\text{O}$

The influence of additional gas streams of 200 ppm  $\text{SO}_2$  and/or 5%  $\text{H}_2\text{O}$  on  $\text{NO}_x$  reduction is investigated. The temperature is kept constant at 350 °C. The  $\text{NO}_x$  reduction is registered some minutes before and after the additional gas streams are turned on and off. The results are displayed in Figure 7. After  $\text{SO}_2$  addition, the  $\text{NO}_x$  conversion decreases from 99% to 95%. When water is added, the  $\text{NO}_x$  reduction decreases to 91% and when  $\text{SO}_2$  and water are added simultaneously, it becomes about 84%. Furthermore, it is observed that the fluctuations of the measured  $\text{NO}_x$  concentrations increase in the following order:  $\text{SO}_2 < \text{H}_2\text{O} < \text{SO}_2$  and  $\text{H}_2\text{O}$ . After the additional gases are turned off, the  $\text{NO}_x$  reduction efficiency returns in all three cases to a value very similar to the initial value.

The  $\text{SO}_2$  and  $\text{H}_2\text{O}$  resistance of the Fe0.5-W-Ce catalyst is cross compared to some experimental values found in literature. The applied operation conditions vary widely. Especially the reaction temperature is reported to have a strong influence. At higher temperatures the impact of  $\text{SO}_2$  and  $\text{H}_2\text{O}$  is less severe than at lower temperatures [38]. As mentioned above the SCR performance of the Fe0.5-W-Ce catalyst is investigated only at 350 °C. Other temperatures should be tested in future experiments. It is often stated that the influence of  $\text{H}_2\text{O}$  is reversible, while the impact of  $\text{SO}_2$  on the reaction is permanent and only partial recovery is possible [39]. Therefore the terms “ $\text{H}_2\text{O}$  inhibition” and “ $\text{SO}_2$  deactivation” are used. This strong influence is not observed in the present study. The  $\text{NO}_x$  conversion decrease is almost 100% reversible after  $\text{H}_2\text{O}$  and/or  $\text{SO}_2$  treatment (Figure 7). Reasons for the good deactivation resistance can be found in the literature. Tungsten [19] and iron [14] are said to enhance the resistance of catalysts. For tungsten oxide, this fact is attributed to its ability to lower the thermal stability of cerium sulfates, which would otherwise block the active sites of the catalyst [21]. Since tungsten and iron are present in Fe0.5-W-Ce, it is assumed that in the current study these effects

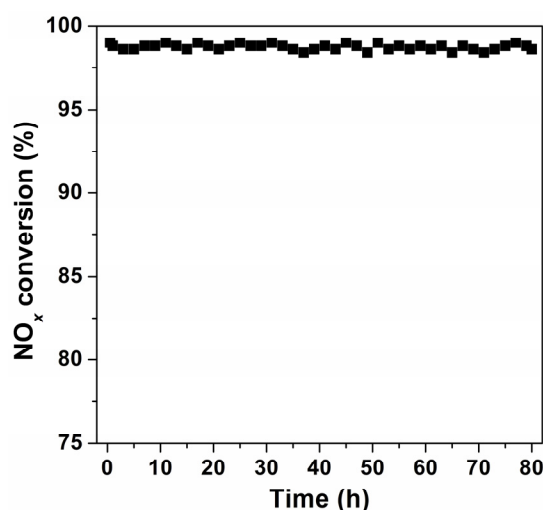


come into operation. Thus, the Fe0.5-W-Ce catalyst shows a very good resistance to SO<sub>2</sub> and H<sub>2</sub>O poisoning, which supports its applicability in a power plant.



**Figure 7.** Influence of H<sub>2</sub>O and/or SO<sub>2</sub> on NO<sub>x</sub> conversion over Fe0.5-W-Ce catalyst. Reaction conditions: [NO<sub>x</sub>] = 450 ppm, [NH<sub>3</sub>] = 450 ppm, 2.5% O<sub>2</sub>, N<sub>2</sub> as balance, GHSV = 20,000 h<sup>−1</sup>.

In the stability test, the SCR reaction showed a stable behavior over 80 h (Figure 8). During the whole period, the NO<sub>x</sub> reduction stays almost constant. It fluctuates between 99.0% and 98.4% with an average of 98.7%. Even though the Fe0.5-W-Ce catalyst shows a very good stability, the desired catalyst lifetime in practical application is thousands of hours—a timespan that can not be tested in laboratory scale experiments. Some researchers predict the deactivation of SCR catalysts by ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) [40]. In the present experiment heating of the gas tubes is applied to exclude liquid water from the reaction and avoid NH<sub>4</sub>NO<sub>3</sub> formation. A physicochemical characterization of the spent catalysts could reveal if ammonium nitrate is nevertheless formed in significant amounts.



**Figure 8.** The long-term stability test on Fe0.5-W-Ce catalyst. Reaction conditions: [NO<sub>x</sub>] = 450 ppm, [NH<sub>3</sub>] = 450 ppm, 2.5% O<sub>2</sub>, N<sub>2</sub> as balance, GHSV = 20,000 h<sup>−1</sup>.

### 3. Discussion

It can be concluded that this Fe<sub>2</sub>O<sub>3</sub> layer covers the catalyst surface and hinders the interaction between the CeO<sub>2</sub>-WO<sub>3</sub> and the reactants in the gas phase (NO, NH<sub>3</sub>). Hints to a highly dispersed form of iron oxide in Fe0.5-W-Ce are given by the XRD, Raman and UV-vis results. The formation of

a solid solution of Fe and Ce as a new active phase can lead to a higher NO<sub>x</sub> reduction efficiency [25]. This can be an explanation why the Fe<sub>0.5</sub>-W-Ce performs better compared to the W-Ce catalyst. The idea that a large amount of Fe<sub>2</sub>O<sub>3</sub> may cover the active sides of WO<sub>x</sub> and CeO<sub>2</sub> in Fe<sub>1</sub>-W-Ce and Fe<sub>2</sub>-W-Ce is supported by the XRD and UV-vis results.

The XRD patterns of the samples after reaction are shown in Figure S2. The characteristic peaks of Fe-W-Ce catalysts are similar with that of the fresh samples (Figure 2), indicating the crystal structure of FeW-Ce are not destroyed after reaction. Furthermore, no significant changes for the characteristic peaks of Fe<sub>0.5</sub>-W-Ce after the experiments of SO<sub>2</sub> and H<sub>2</sub>O resistance are observed (Figures S3 and S4), suggesting the Fe<sub>0.5</sub>-W-Ce could possess the high stability. Nevertheless, the catalyst after the experiments of SO<sub>2</sub> and H<sub>2</sub>O resistance results in a decrease in surface area (Table S1). The decrease in BET surface area is primarily due to the surface sulfate species formation.

At the first glance, the weak SCR performance of Fe<sub>1</sub>-W-Ce and Fe<sub>2</sub>-W-Ce samples seem to be contradictory to its high specific surface area. However, as mentioned before, the direct neighbors of each atom in a crystal lattice are more important for the SCR than the overall crystallinity [21]. In the next step, the SCR performance of the novel catalysts shall be compared to previous studies. For this task, three criteria are chosen: the NO<sub>x</sub> conversion, the lowest operation temperature, and the size of the operation temperature window. It is important to define the term “operation temperature” as it is used in this study. Two definitions for low temperature SCR applications exist in literature: some researchers claim that the operation temperature window comprises the temperature range where the NO<sub>x</sub> reduction is >80% [41]. Other research groups set a threshold of >90% NO<sub>x</sub> reduction [25]. Because stricter legal regulations for NO<sub>x</sub> emissions can be expected in the future the value of 90% is used in this study. The lowest operation temperature should be in the ideal case <200 °C, since this is the temperature of the flue gases at the tail-end of a power plant.

Firstly, catalysts that contain only cerium and tungsten oxides shall be compared. Our W-Ce catalyst reaches the threshold of 90% NO<sub>x</sub> reduction at 230 °C and slightly misses the ideal operation temperature of <200 °C. The maximum NO<sub>x</sub> reduction for these catalysts is 99%. The catalysts of other research groups show a similarly high efficiency (Table 2). Peng et al. reached the 90% mark at 185 °C [42], Ma et al. at 190 °C [33], Shan et al. at 215 °C [17] and Liu et al. at 290 °C [43]. It has to be kept in mind that different preparation techniques and operation conditions have been used. Roughly speaking, the W-Ce catalyst achieves average performance results. Considering the iron oxide catalysts, Fe<sub>0.5</sub>-W-Ce achieves a NO<sub>x</sub> reduction >90% at 200 °C and a maximal NO<sub>x</sub> reduction of 99%. It therefore fulfills the criteria set for a low temperature SCR catalyst. In literature one finds iron oxide catalysts with >90% NO<sub>x</sub> reduction at 150 °C [13] and at 350 °C [35]. Another Fe catalysts prepared by the sol-gel method only reaches 55% maximal NO<sub>x</sub> reduction [14].

**Table 2.** Comparison of the activity for NH<sub>3</sub>-SCR on different catalysts.

| Samples                              | Reaction Conditions   | Temperature (°C) | NO <sub>x</sub> Conversion (%) | References |
|--------------------------------------|---|------------------|--------------------------------|------------|
| Fe <sub>2</sub> O <sub>3</sub>       | 500 ppm NO, 500 ppm NH <sub>3</sub> ,<br>3% O <sub>2</sub> , and balance N <sub>2</sub>                   | 150              | 90                             | [13]       |
| Fe-Mn-Ce/TiO <sub>2</sub>            | 0.06 vol % NO, 0.06 vol % NH <sub>3</sub> ,<br>3 vol % O <sub>2</sub> and pure N <sub>2</sub> in balance  | 180              | 96                             | [14]       |
| Ce-W                                 | 500 ppm NO, 500 ppm NH <sub>3</sub> ,<br>5 vol % O <sub>2</sub> , balance N <sub>2</sub>                  | 215              | 90                             | [17]       |
| WO <sub>3</sub> /CeO <sub>2</sub>    | 500 ppm NO, 500 ppm NH <sub>3</sub> ,<br>5% O <sub>2</sub> and N <sub>2</sub> in balance                  | 190              | 90                             | [33]       |
| Co/Fe <sub>2</sub> O <sub>3</sub>    | [NO] = 500 ppm, [NH <sub>3</sub> ] = 500 ppm,<br>[O <sub>2</sub> ] = 2 vol %, balance gas: N <sub>2</sub> | 350              | 90                             | [35]       |
| Mn-CeO <sub>2</sub> -WO <sub>3</sub> | 0.05% NO, 0.05% NH <sub>3</sub> , 3% O <sub>2</sub> ,<br>and in a N <sub>2</sub> stream.                  | 185              | 90                             | [42]       |
| CeO <sub>2</sub> -WO <sub>3</sub>    | 500 ppm NO, 500 ppm NH <sub>3</sub> ,<br>3 vol % O <sub>2</sub> and balance in N <sub>2</sub>             | 290              | 90                             | [43]       |



## 4. Materials and Methods

### 4.1. Catalyst Preparation

Four W-Ce catalysts doped with different amounts of Fe were prepared by the sol-gel method. First an appropriate amount of ammonium tungstate was added to deionized water under continuous stirring. To dissolve the ammonium tungstate, an equal amount of oxalic acid dihydrate was added and the solution was mixed until it became clear. The molar ratios were Fe/W/Ce = 0:1:1, 0.5:1:1, 1:1:1 and 2:1:1. The  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was the source of iron and Cerium, respectively. As complexing agent citric acid was added in a molar ratio of 1.3:1 to all metal ions. Last polyethylene glycol (PEG) was added in an amount corresponding to 50% (*w/w*) of citric acid. Afterwards, the samples were heated to 80 °C under ongoing stirring until the gel formation was completed. The gel was then put to a furnace at 120 °C until the gel was dry. Subsequently, the samples were calcined at 500 °C for 3 h. After calcination, the catalysts were pressed, crushed and sieved to 20–40 mesh. The catalysts are denoted as  $\text{Fe}_x\text{-W-Ce}$ , and  $x$  stands for the molar ratio of Fe to W.

### 4.2. Catalyst Characterization

The specific surface areas were obtained from  $\text{N}_2$  adsorption/desorption isotherms measured on a Micromeritics ASAP 2020 M (Quantachrome, Boynton Beach, FL, USA) at  $-196^\circ\text{C}$ , then are calculated using the Brunauer–Emmett–Teller (BET) method. The ICP-AES was used to determine the molar ratio of Fe/W/Ce in the synthesized samples, which was performed on an OPTIMA 2000 (PerkinElmer, Waltham, MA, USA). The XRD patterns of catalysts were collected on a Bruker AXS-D8 Advance powder diffractometer (Bruker, Karlsruhe, Germany) with a  $\text{Cu K}\alpha$  radiation source of wavelength 1.5406 Å, and the crystallite size was calculated by the main peak at  $28.7^\circ$  according to Scherrer's equation. UV Raman spectra were recorded on a DXR Microscope Raman spectrograph (ThermoFisher Scientific, Waltham, MA, USA) with He-Cd laser of 325 nm excitation wavelength. The UV-vis diffuse reflectance spectroscopy (DRS) was carried out on a Hitachi U-4100 UV/Vis/NIR spectrophotometer (Hitachi, Tokyo, Japan), and wavelengths from 200 to 800 nm were scanned for light absorption.

### 4.3. Activity Measurement

The  $\text{NH}_3$ -SCR activity was performed in a fixed bed reactor using a MRU vario plus industrial flue gas measurement device. The Fe-W-Ce catalyst (0.3 g, 20–40 mesh) was mixed with silica sand (0.4 g, 20–40 mesh), and then filled into a quartz reactor with 8 mm inner diameter. The reaction conditions were controlled as follows: 450–500 ppm  $\text{NO}_x$ , 450–500 ppm  $\text{NH}_3$ , 2.5%  $\text{O}_2$ ,  $\text{N}_2$  as balance. Before the activity test, the measured values of the gas concentrations were allowed to stabilize at room temperature for around 1.5 h. Each temperature was kept until the measured values stabilize (40–60 min).

## 5. Conclusions

The investigation of the SCR performance reveals a good  $\text{NO}_x$  conversion and high resistance to differences in operation parameters as well as to poisoning by flue gas compounds. In comparison to the literature, the very wide operation temperature window of the W-Ce and the Fe0.5-W-Ce catalyst is remarkable. A  $\text{NO}_x$  reduction of >90% is reached over a span of 260 °C for W-Ce and over a span of 290 °C for Fe0.5-W-Ce. This indicates that the newly developed catalysts can be used in low temperature SCR as well as at higher temperatures. They are very flexible in application.

**Supplementary Materials:** The following are available online at [www.mdpi.com/2073-4344/7/2/71/s1](http://www.mdpi.com/2073-4344/7/2/71/s1), Figure S1: The  $\text{N}_2$  adsorption-desorption isotherms of Fe-W-Ce catalysts, Figure S2: XRD patterns of Fe-W-Ce catalysts after reaction, Figure S3: XRD patterns of Fe0.5-W-Ce catalysts after reaction (a:  $\text{SO}_2 + \text{NO}_x + \text{NH}_3 + \text{O}_2$ , b:  $\text{SO}_2 + \text{NO}_x + \text{NH}_3 + \text{H}_2\text{O} + \text{O}_2$ ), Figure S4: Raman patterns of Fe0.5-W-Ce catalysts after reaction (a:  $\text{SO}_2 + \text{NO}_x + \text{NH}_3 + \text{O}_2$ ,

b:  $\text{SO}_2 + \text{NO}_x + \text{NH}_3 + \text{H}_2\text{O} + \text{O}_2$ ), Table S1: Specific surface area and crystallite size of Fe<sub>0.5</sub>-W-Ce catalysts after reaction.

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