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Multi-component Zirconia-Titania Mixed Oxides: Catalytic Materials with Unprecedented Performance in the Selective Catalytic Reduction of NO_x with NH₃ after harsh hydrothermal ageing.

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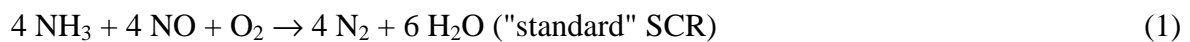
Abstract. Standing harsh hydrothermal treatment (~ 10% H₂O, ~ 1050 K) is a prerequisite for deNO_x catalysts of tomorrow in Diesel exhaust gas treatment. New catalytic materials composed of Mn-, Fe- and Ce-ZrTiSiW mixed oxide were evaluated in the selective catalytic reduction NO by NH₃ at high gas hourly space velocity (330,000 mL g⁻¹ h⁻¹) and after high temperature hydrothermal treatment, 16 h at 1023 K in H₂O/air (10/90). They were compared with a Fe-ZSM5 SCR catalyst treated in the same manner. CeZrTiSiW exhibits the best performance and keeps high NO conversion (> 80%) from 630 to 800 K. It is stable and fully selective to N₂ up to 823 K. It is more active and selective than Fe-ZSM5. The presence of

NO_2 in the feed ($\text{NO}_2/\text{NO} = 0.85$) boosts the NO conversion by shifting the light-off temperature (50% NO conversion) from 560 K to 460 K.

Keywords. DeNOx, nitrogen oxide, mixed oxide, cerium, zirconia, selective catalytic reduction.

1. Introduction.

The abatement of nitrogen oxides (NOx) and particulate matter (PM) emissions from exhaust gases of diesel and lean-burn gasoline engines represents a significant challenge for further development of these vehicles [1-4]. Pollutant emissions of these engines are currently four to five higher than for gasoline engines. The current Euro 5 and TIER4 emissions standards require diesel emissions to be equivalent to gasoline vehicles. Towards this goal, car manufacturers are confident they can use diesel engine technologies, e.g. exhaust gas recirculation ..., to meet the standards with engine-out emissions. However, the Euro 6 standard (2014) will require significant NOx emission abatement and use of an exhaust gas aftertreatment seems unavoidable. Among potentially implementable technologies, the selective catalytic reduction (SCR) by urea attracts most attentions now [3]. Within the SCR system, the reduction of NO and/or NO_2 is accomplished by reaction with NH_3 (formed onboard from urea) in the presence of O_2 as follows:



The vast majority of truck manufacturers currently make SCR-equipped vehicles. The SCR process by NH_3 using vanadium-titanium mixed oxide catalyst (V-Ti) is one of the best control technology to remove noxious NO_x from power plants and some industrial

applications [5]. The V-Ti catalysts are very efficient in the range 523-623 K and they were later applied to SCR-urea systems for automotive catalytic converters [3]. However, V-Ti based materials, even promoted with W and Mo, suffer from some drawbacks: (i) they do not generally exhibit a sufficient activity at low temperature (< 523 K), (ii) the direct oxidation of NH_3 by O_2 becomes significant at high temperature (> 623 K), (iii) there is unselective reduction of NO to N_2O , and (iv) the toxicity of vanadium is a concern for automotive applications. For these reasons, more active, selective and ecofriendly catalytic formulations for NH_3 -SCR are in high demand. Fe- and Cu-based zeolite catalysts show improvements in these areas and have been applied to automotive applications [6-9]. However, the stability of the catalytic body under severe hydrothermal treatment (> 950 K) and transient conditions in vehicle applications is a key concern. Indeed, thermal stability is now even more critical as the use of catalytic diesel particulate filters (CDPF) becomes required by the newest regulations. The periodic regeneration of the CDPF is triggered by a rise of the temperature above 900 K, which impacts the stability of the different catalytic monoliths along the exhaust line [10]. Moreover, this periodic regeneration of CDPF increases the fuel consumption and CO_2 emissions. For some car manufacturers, a long-term strategy based on SCR technology and small additional CO_2 emissions is to reduce the NO_x end-of pipe emissions while maintaining high NO_x raw emissions [11]. From these points of view, it is necessary to design hydrothermally stable materials. Some recent examples of up-to-date formulations composed of Fe and/or Cu within ZSM-5, beta, SSS-13 and chabazite as zeolites address this point [12-17]. However, it remains of concern to design new catalysts based on different materials offering alternative to Fe- and Cu-based formulations. Actually, some questions remains about the possible formation of dioxins with unburned hydrocarbons on Cu-based catalysts [18].

A new class of zirconia-based mixed oxides with promising deNO_x properties has emerged from our experience with hydrothermally stable zirconia-based materials for gasoline engine aftertreatment [19,20]. Guidelines for choosing promoters for zirconia-based materials have also been developed, with particular interest in the following characteristics: i) high temperature phase stability (> 1200 K), ii) acidity, iii) redox properties, and iv) no vanadium. Specifically, Si, Ti and W have been added for thermal stability and acidity, while Ce, Fe or Mn are included to enhance redox properties [21-27]. The catalytic properties of these mixed oxides were evaluated in the SCR of NO by NH₃ and compared with Fe-ZSM-5 and a commercial V₂O₅-WO₃/TiO₂ SCR catalyst (V-Ti), after hydrothermal ageing at 1023 K.

2. Experimental.

2.1. Materials

The promoted zirconia materials investigated in this paper have been prepared using a patented MEL Chemical-Rhodia process [19].

As an example, the synthesis of CeZrTiSiW mixed oxide is described in the following. A solution was prepared by mixing with stirring 134.5 g zirconyl chloride, 86.5 g titanyl chloride, 20 g cerium(III) nitrate, 22 g sulfuric acid (97 wt%) with 90 g distilled water. This solution was gradually added into a stirred reactor containing 661 g of a sodium hydroxide solution (10 wt% NaOH). The pH of the medium was adjusted to 12.5 by adding a solution of sodium hydroxide. 8 g of hydrogen peroxide (30 vol%) were then introduced into the medium. After stirring for 30 min, the precipitate obtained was filtered and washed at 60° C with distilled water (3 L). The solid was put back into suspension in 1 L distilled water. A solution of 10 g sodium silicate (232 g L⁻¹ SiO₂) and 5.9 g sodium metatungstate dihydrate in 13 g distilled water was introduced into this suspension with stirring. The pH was adjusted to 4 by addition of a HNO₃ solution (68 vol%). The medium was brought to 60° C for 30 min,

then the precipitate was again filtered and washed at 60° C with 3 L distilled water. The as synthesized material was calcined at 823 K in flowing air for 24 h, then hydrothermally aged at 1023 K in H₂O/air (10/90) for 16 h. The final material contained less than 120 ppm sulfates, 50 ppm sodium and 10 ppm chlorides.

Fe-ZSM-5 was prepared by impregnation of ZSM-5 (Si/Al = 16.6) with iron acetylacetonate [28,29]. Briefly, a solution of iron(III) acetylacetonate (Aldrich, 0.309g) in H₂O/CH₃CN (75/25, 90 mL) was dropwise added to a suspension of ZSM-5 (Si/Al = 16.6, 2.2g) in H₂O/CH₃CN (75/25, 15 mL). The mixture was stirred one night under reflux. The same impregnation procedure was repeated twice on the solid recovered by centrifugation. The solid was dried one night at 100°C, calcined at 773 K in air. Fe loading reach 2.13 wt% as given by elemental analysis (Service Central d'Analyse CNRS, Solaize, France). This catalyst and the commercial V-Ti SCR catalyst were subjected to the same ageing treatment as the Zr-based mixed oxides.

The materials were characterized by N₂ sorption, XRD and temperature desorption of NH₃.

The N₂ sorption isotherms were determined at 77 K on a Micromeritics ASAP 2010 apparatus on 40 to 50 mg samples previously heated overnight at 150°C under vacuum. XRD pattern were recorded on a Bruker D8 Advance diffractometer equipped with a copper anod, operating at 40 kV and 50 mA.

The number of acid sites was evaluated by temperature-programmed desorption (TPD) of ammonia using an AUTOCHEM 2910 (Micromeritics). Before NH₃ adsorption, the sample (0.1 g) was pre-treated in air flow (30 mL min⁻¹) at 723 K (ramp 10 K min⁻¹) for 30 min. NH₃ adsorption was done at 373 K by exposition to NH₃/He (5.0/95.0, flow rate: 30 mL min⁻¹) for 45 min and then flushed with He (30 mL min⁻¹) during 2 h to remove NH₃ remaining in the gas phase and physisorbed on the catalyst surface. Finally, ammonia was desorbed in helium

flow (30 mL min⁻¹) from 373 to 923 K at a heating rate of 10 K min⁻¹ and quantified with a thermal conductivity detector (TCD).

2.2. Catalytic experiments

The SCR experiments were carried out in a flow quartz reactor operating at atmospheric pressure. Catalyst aliquots (20 mg diluted in 180 mg SiC) were activated in situ at 773 K in O₂/He flow (10/90, 60 mL min⁻¹) for 1 h and then cooled down to 423 K. The catalytic tests were then started in the temperature-programmed reaction mode (TPSR) from 423 to 823 K at 5 K min⁻¹. Composition (mol%) of the feed gas was 500 ppm NO, 500 ppm NH₃, 2 vol% H₂O, 8 vol% O₂ and balance He, flow rate 110 mL min⁻¹. The gas hourly space velocity (GHSV) was about 330,000 mL g⁻¹ h⁻¹. The effluent composition was continuously analyzed on-line by quadrupole mass spectroscopy.

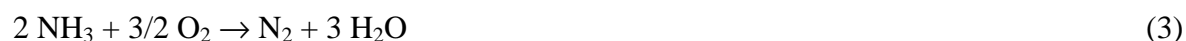
3. Results and discussions.

Table 1 shows the main characteristics of the catalysts. The zirconia-based mixed oxides exhibit a modest surface area, while Fe-ZSM-5 starts out much higher (~ 300 m² g⁻¹). XRD of the zirconia-based mixed oxides show that ZrTiO₄ as major phase and anatase TiO₂, CeO₂ or WO₃ as minor component may be identified after hydrothermal aging (Figure S1, supporting information). None of the mixed oxides showed evidence of clear diffraction lines for the simple oxides CeO₂, Mn₂O₃ or Fe₂O₃, suggesting that these elements are incorporated within or are finely dispersed in the zirconia matrix. For Fe-ZSM-5 material, the diffraction lines of the MFI structure were visible with some amounts of amorphous phase (Figure S2, supporting information). The acid properties of the materials were evaluated by temperature programmed desorption of NH₃ (NH₃-TPD). The data for all catalysts show only a single peak of NH₃ desorption with maximum at ca 460-480 K, which is typical of materials with

medium acid strength (Figure S3, supporting information). Due to the fact that ammonia desorption takes place over a wide temperature range with skewing, the average temperature of NH_3 desorption, taken as the first moment derived from the TPD curve, was chosen as the key metric. In this case, all the catalysts exhibit similar strength of the acid sites and CeZrTiSiW shows higher sites number than either FeZrTiSiW or MnZrTiSiW, and similar to Fe-ZSM-5. It is well known that SCR on mixed oxides and transition metal in zeolites follow a complex catalytic cycle involving both acid and redox sites. For instance, it was well demonstrated that the SCR mechanism obeys to a cooperative effect between acid and redox sites on V-Ti catalysts [30]. TPD- NH_3 is thus a key protocol as it provides evidence of acid sites and shows that both CeZrTiSiW, FeZrTiSiW and MnZrTiSiW may be promising for SCR, with combination of acidity and redox properties (Fe, Mn, Ce).

Results of the SCR experiments are shown in Figure 1. FeZrTiSiW is found less active than CeZrTiSiW in the whole range of temperatures. CeZrTiSiW and MnZrTiSiW exhibit similar activity below 523 K, but show some divergence at higher temperatures. CeZrTiSiW shows better performance than MnZrTiSiW, since NO conversion decreases sharply above 673 K for the latter. This decrease in NO conversion is likely caused by NH_3 oxidation to N_2 , NO and N_2O ; N_2O reaching 70 ppm at 773 K. In contrast, CeZrTiSiW shows ~ 20% NO conversion as early as 523 K with a maximum above 75% at 600-800 K. Further, no detectable N_2O formation (~ 99% N_2 selectivity) was observed. The deNO_x activity of CeZrTiSiW is also better than that of the reference Fe-ZSM-5 over all the temperature range (Figure 1). It is worth noting that the V-Ti catalyst exhibits very poor performances after hydrothermal treatment at 1023 K in wet air. Moreover, in a dry feed (except the presence of H_2O formed in the course of the reaction), the NO conversion on CeZrTiSiW peaked at 92% at 753 K, and maintained at $84\pm 1\%$ from 2 to 5% H_2O .

Figure 1 only shows the NO conversion as a function of temperature. For a better insight in the comparison between CeZrTiSiW and Fe-ZSM-5, Figure 2 presents the conversions of the reactants NO and NH₃, as well as the amounts of products N₂ and N₂O. In agreement with equation 1, the NO conversion and the N₂ yield correspond well up to 700 K. In contrast, the NH₃ conversion is lower than expected. This behaviour may be due to the operating mode of the SCR test with a steady increase of temperature, which does not allow to reach perfect steady-state conditions. A catalytic test was done with CeZrTiSiW by decreasing steps from 673 to 523 K (Figure S4, supporting information). The NO and NH₃ conversions are then very close. The CeZrTiSiW catalyst was also submitted to a long-lasting run at 693 K (Figure 3). This experiment shows: i) that during the 50 h reaction the NO and NH₃ conversions fit very well the N₂ formed, ii) the excellent stability of the catalyst, and iii) that N₂O is not formed. On this last point, CeZrTiSiW, which does not produce any N₂O in the whole temperature range studied, offers a striking advantage against Fe-ZSM-5, which yields 80 ppm N₂O at 823 K (Figure 2). Above 700 K, there is a clear splitting of NO and NH₃ conversions on both catalysts (Figure 2). This is due to the consumption of NH₃ in the unselective catalytic oxidation to N₂ (equation 3), which then becomes significant (Figure S5, supporting information).



Interestingly, a WO₃/CeO₂-ZrO₂ catalyst was recently claimed as promising for the SCR of diesel exhaust [25], which exhibited ~50% NO conversion at 523 K and GHSV of 60,000 mL g⁻¹ h⁻¹ after dry calcinations for 4 h at 1073 K. Assuming the classical first-order dependence of SCR rate with respect to NO partial pressure, a 50% NO conversion at 60,000 mL g⁻¹ h⁻¹ corresponds to ~12% at 330,000 mL g⁻¹ h⁻¹. The data shown here suggests that CeZrTiSiW would be twice as active as WO₃/CeO₂-ZrO₂. Moreover, a water free treatment at high temperature is much less severe ageing than a hydrothermal treatment for the catalytic

properties of the materials. The effect of dry or wet atmosphere during the thermal treatment of CeZrTiSiW is shown in Figure S6 (supporting information). The maximum of NO conversion increases from 81 to 88% when the precursor catalyst is treated at 1023 K in dry air.

NO₂ will be likely present in the real exhaust gas from Diesel cars [11]. NO₂ has a positive effect on the deNO_x rate thanks to the occurrence of the "fast SCR" (equation 2). We thus processed a NO_x feed containing 270 ppm NO and 230 ppm NO₂ with 500 ppm NH₃, 8% O₂ and 2% H₂O on CeZrTiSiW. Figure 4 shows the clear positive effect of the presence of NO₂ with a down shift of the light-off temperature (50% NO_x conversion) from 560 K (NO alone) to 460 K (NO+NO₂). The overall NO+NO₂ conversion maintains above 90% from 500 to 750 K, and the N₂O formation does not exceed 10 ppm at 823 K. To the best of our knowledge, CeZrTiSiW can be ranked as the best reported performing hydrothermally aged mixed oxide catalyst, which may be compared with up-to-date zeolite-based formulations.

4. Conclusions.

In summary, this study shows that after severe hydrothermal ageing of Fe-, Mn- and Ce-ZrTiSiW mixed oxides, CeZrTiSiWO_x is the most promising catalytic composition for the SCR of NO by NH₃, which exhibits high NO conversion from 523 to 823 K, larger than for the reference Fe-ZSM-5 catalyst. DeNO_x through the SCR process is a promising area for the discovery of new materials with improved efficiency and stability after severe hydrothermal treatments. CeZrTiSiW mixed oxides constitute a new class for these catalysts, showing performances which may compete with those of Cu- and Fe-zeolite. Additionally, these materials are very stable, highly active after hydrothermal ageing at 1023 K, and have undetectable N₂O formation. There is now a need to understand the role of each component in

order to design optimised composition for cars complying with the very drastic regulations of EURO6 directive.

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