1 Catalyst Design for Mitigating Nitrosamines in CO₂

2 Capture Process

3
4 *Payal Chandan, Sarah Honchul, Jesse Thompson, Kunlei Liu*

5
6 Center for Applied Energy Research, University of Kentucky,

7 2540 Research Park Drive, Lexington, KY-40511

8 GRAPHICAL ABSTRACT

ABSTRACT

Nitrosamines formation during amine based CO₂ capture process has recently gained strong attention due to potential health and environmental concerns. In this paper, catalytic nitrosamine destruction in aqueous amine solutions with amine recovery approach is proposed. An up-flow fixed-bed reactor was designed for laboratory experiments in which a nitrosamine solvent stream along with hydrogen was passed into the reactor over a selected catalyst bed. A number of Pd, Fe and Ni metal catalysts were synthesized based on metal-support interaction and were evaluated towards nitrosamine hydrogenation. The Ni based catalyst was found to possess excellent activity (>95%) towards the destruction of 100 mg/L nitrosopyrrolidine in 5 mol/kg MEA solution at 120 psi hydrogen pressure and 120 °C temperature in 4 h. Catalyst reusability study was conducted for 15 cycles showed high catalyst activity and stability lasting more than 60 h. This catalyst was prepared by incipient-wetness technique and was characterized by SEM, TPR, N₂ adsorption-desorption and XRD to determine its intrinsic structural properties. The catalyst was further studied with several different nitrosamines to prove its utility towards multiple nitrosamines.

KEYWORDS

CO₂ capture, Hydrogenation, Nickel catalyst, Nitrosamines, Solvent recovery approach

1. INTRODUCTION

Post-combustion CO₂ capture using aqueous amines is currently considered the most mature method to control CO₂ emission from power plants. During this process, amines are involved in complex chemical reactions and can form new degradation compounds, which could potentially affect the environment. Many amine capture systems rely on using secondary amines as the solvent. However, a major drawback of using secondary amine is potential formation of carcinogenic nitrosamines (Challis et al., 1982). Nitrosamines have recently gained public attention as a possible health hazard. To reduce the public concern, post-combustion CO₂ capture units that use amine based carbon capture technologies will need to demonstrate mitigation strategies for nitrosamines before commercial scale deployment can be realized. The overview of nitrosamines levels observed at CO₂ capture facilities either as gaseous emissions, in liquid blow down of water wash, or in the amine solution is listed in Table 1 (Aas and da Silva, 2010; da Silva et al., 2013; Fostas et al., 2011; Graff, 2010; Rochelle et al., 2013; Shah et al., 2012; Strazisar et al., 2003).

Methods of destroying nitrosamines include: ultraviolet (UV) irradiation (Knuutila et al., 2013; Shah et al., 2013), thermal treatment (Chandan et al., 2013; Fine and Rochelle, 2013; Rochelle et al., 2013), and hydrogenation. Several inhibitors have also been studied to prevent the formation of nitrosamines under CO₂ capture conditions (Chandan et al., 2014 b,c). The rate of destruction through thermal treatment is not controllable since the absorber and stripper conditions are optimized based on the solvent operating conditions. Irradiating the amine solvent with UV would generate a large number of free radicals and increases amine degradation, and therefore UV approach is only applicable to a water wash column.

Nitrosamines could also be reduced by zinc in acetic acid, sodium amalgam, tin in hydrochloric acid, aluminum and lithium aluminum hydride (Fridman et al., 1971; Gangolli et al., 1974; Magee et al., 1976). However, addition of these reagents to the process solution would not be feasible because they could result secondary environmental impacts. Perhaps the most appropriate method for reduction of nitrosamines may be heterogeneous catalytic reduction that does not require addition of any external reagent to the solution. Nitrosamines are hydrogenated to the corresponding hydroxylamines initially, followed by further reduction to regenerate the parent amine (Scheme 1).

Scheme 1: Hydrogenation of nitrosamines

For the proposed nitrosamine destruction concept, experiments were conducted using a fixed-bed reactor with liquid recirculation under operating conditions found in CO₂ capture units. The reactor was designed for screening the prepared catalysts on lab scale. During the experimental runs, liquid samples were collected at different time intervals to analyze the content of nitrosamines compared to the initial solution. Nitrosopyrrolidine (NPy) was chosen as a representative compound from the class of secondary amines nitrosamines due to its commercial availability and well-established GC/MS analysis method. Palladium based heterogeneous catalysts were initially screened for their nitrosamine destruction performance, followed by nickel and iron based catalysts. One important aspect of the catalyst synthesis that was evaluated in detail was to obtain a strong metal-support interaction to maintain catalyst durability. The most promising catalyst, Ni-ZrO₂ was tested without regeneration or reactivation for 15 cycles

providing excellent catalytic activity towards reducing nitrosamines back to amines. This catalyst was characterized by Scanning Electron Microscope (SEM), Temperature Programmed Reduction (TPR), X-Ray Diffraction (XRD), and N₂ adsorption-desorption measurements. This selected catalyst was then evaluated over a mixture of nitrosamines containing solution.

2. MATERIALS AND METHODS

2.1 Chemicals

Zirconyl oxychloride, nickel nitrate hexahydrate, methanol, and ammonium hydroxide were purchased from Fisher Scientific. NPy and nitrosomorpholine (NSMO) were procured from Sigma-Aldrich. Nitrosopiperazine (NPz) and nitrosodiethanolamine (NDELA) were purchased from Fisher Scientific. Monoethanolamine (MEA, >98%) was obtained from UNIVAR. Nitrogen and hydrogen gas cylinders (>99.999% purity) were purchased from Scott-Gross. Standard solution at 1000 mg/L for each metal (Fe, Ni, Pd, Zr) for Inductively Coupled Plasma (ICP) analysis was obtained from Environmental Express.

2.2 Experimental setup and reaction procedure

An up-flow fixed-bed reactor was designed (Figure 1) in which a nitrosamine solvent stream along with hydrogen was passed into the reactor over the catalyst bed. The setup consists of 2 gas cylinders (nitrogen and hydrogen), reservoir, reactor, pump, pressure gauge and sample valves. The reactor was 15" long and 1.84" in diameter. It contained 2 frits to form fixed catalyst bed, one movable frit on top and another at 2" from the bottom. The reactor has 2 K-type thermocouples, 1" from top and other at 3" from bottom. Total volume of the reactor was 180 mL. The reactor has 2 inlets at the bottom for liquid-in and gas-in, and it has 2 outlets, top outlet

for releasing gas and side outlet for liquid circulation. The reservoir holds a total volume of 1.0 L. It has a dip tube of 11" to separate the gas and the liquid. The gas is circulated back into the reactor through the bottom inlet and the liquid is circulated in to the reactor through the pump. Complete system is wrapped with a thin layer of glass wool electric insulation, then heating tape, and again glass wool to maintain the desired temperature. The system also consists of two sample valves one at the bottom of the reactor and another at the top of the reactor.

2.3 Reaction procedure

For a typical experiment, the reactor was filled with 10 g catalyst sandwiched between the layers of glass wool and glass beads on both the sides. The reservoir was filled with 500 mL of a 5 mol/kg MEA solution containing 100 mg/L NPy. Nitrogen gas was passed through the system for 5 min to remove air and then hydrogen gas was passed through the system. The system was pressurized with 120 psi hydrogen pressure and then the temperature was raised to 120 °C. Once the temperature was reached, the liquid circulation pump was started to flow the liquid at the rate of 30 mL/min, corresponding to a liquid hourly space velocity (LHSV) of 0.3 h⁻¹. A measured amount of sample was taken every 2 h and analyzed by GC-MS to determine nitrosamine concentration. The fresh catalyst was activated at 150 °C and 120 psi hydrogen pressure in the same reactor for 6 h prior to the experimental run. After the run was over, the reactor and reservoir were cooled, the pressure was released and the reaction solution was removed completely. The reservoir was detached, washed with DI water. The reservoir was again filled with DI water, reconnected and the water was circulated several times to clean the reactor and wash any adsorbed species from the catalyst surface. For the multi-cycle investigations, the catalyst(s) were used without reactivation in subsequent experiments.

129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150

2.4

Catalysts synthesis procedure

Hexagonal mesoporous silica (HMS) was prepared using a reported procedure (Yadav et al., 2012). For synthesis of Ni-ZrO₂ catalyst, zirconium oxychloride was dissolved in 250 mL deionized (DI) water. The solution was stirred and ammonia was added over it for 15-20 min. The resultant precipitate of zirconium hydroxide was agitated for 18 h at room temperature. The residue was filtered under vacuum and washed with DI water until neutral pH was obtained. The obtained Zr(OH)₄ was dried in the oven at 100 °C for 24 h.

Nickel in the form of nickel nitrate was loaded over HMS or zirconium hydroxide by wet impregnation method using methanol as a solvent and dried until a free flowing powder was obtained. Both the catalysts were then calcined and the powder form was pelletized using sodium silicate as a binder before loading in the reactor.

2.5 GC-MS for liquid sample analysis

The analysis was conducted on Agilent GC-MS instrument equipped with DB-624 capillary column 0.25mm i.d.×30m length using 1 mL/min helium flow rate. Masses were scanned in the range of 50-500 amu. Split ratio was 20:1. The samples were extracted in DCM prior to the analysis using NSMO as an internal standard. The change in the relative response factor of NPy to the NSMO was monitored over the reaction time to determine the percent nitrosamine destruction.

2.6 Catalyst characterization

Catalyst characterization was performed using ICP, SEM, TPR, N₂ adsorption desorption and XRD. In detail, ICP testing was performed using a Varian 720ES instrument to determine the bulk metal content in the OMS based catalyst. Approximately 0.05 g of each catalyst was digested in trace metal grade nitric acid at 110 °C and then diluted to 50 mL in DI water. One blank and one laboratory controlled sample was also treated in the similar manner for quality control. The diluted samples were then filtered under vacuum and 10 mL was transferred into the analysis vial. For each metal ion, five calibration standards (1, 5, 10, 50, 100 mg/L) were prepared. For each element at least 3 wavelengths were chosen such that it does not interfere with other elements of interest. Yttrium solution was used as an internal standard.

BET surface area for each sample was determined by N₂ adsorption-desorption using Micromeritics (USA) ASAP 2020 unit. The surface area and porosity were measured using ~150 mg of powder sample after degassing at 160 °C for 4h. SEM analysis was performed after coating the sample with gold using a Hitachi S-4800 instrument operating at 20 kV electron detector. Powder XRD was obtained from Rigaku instrument at the scan rate of 0.5 °/min in the 2θ scan range of 5 to 120° for ZrO₂ and Ni-ZrO₂. TPR analysis was conducted using Micromeritics in the presence of 1 mL/min hydrogen flow rate at the scan rate of 5 °C/min upto 1000 °C.

3. RESULTS AND DISCUSSION

3.1 Contribution from thermal decomposition

Under the studied experimental conditions, thermal decomposition of nitrosamines is likely to occur in parallel to the main hydrogenation reaction (Chandan et al., 2013; Fine and Rochelle, 2013; Rochelle et al., 2013). Here, the contribution from thermal decomposition was calculated

from the blank run i.e. NPy destruction under 120 psi nitrogen atmosphere without catalyst. About 15% conversion was obtained in 4 h at 120 °C. The contribution to the reaction by thermal decomposition is represented in Figure 2.

3.2 Catalyst design and evaluation

Discussion on each catalyst given below represents the total destruction of nitrosamines that includes catalytic hydrogenation and contribution from thermal decomposition (Figure 3). Detailed study has been conducted to find the most appropriate catalyst for the process. Regeneration of amine (pyrrolidine) under hydrogenation condition was confirmed by GC-MS analysis.

A well-known hydrogenation catalyst Pd (Cerveny, 1989) was chosen for initial screening at 50 °C and 50 psi pressure for 100 mg/L NPy solution in DI water. Synthesis of this catalyst was recently reported (Chandan et al., 2014a). The conversion of NPy to Py of 92% in the first cycle was dropped to 44% for the 6th cycle for 2% Pd-silica granules. The loss in the activity after recycling the catalyst could be due to metal leaching from the support surface. After the proof of concept experiments with Pd catalysts, the focus was shifted to make nickel or iron based cost-effective catalysts. The Ni supported on silica granules catalyst was tested at 100 °C and 100 psi for 6 cycles, activity again dropped in subsequent cycles from the highest value of 52%. For a few catalysts tested here, the destruction capacity increases for the second cycle; likely due to insufficient catalyst activation in the first attempt.

Next, manganese octahedral molecular sieve (OMS-2) based metal (e.g. Pd, Fe and Ni) catalysts were tested at 120 °C and 120 psi. The synthesis and a brief discussion about these catalysts was recently published (Chandan et al., 2014a). During synthesis potassium ions inside

the tunnel are replaced with active metal and the metal deposition depends on its size compatibility with tunnel. These catalysts are known for their redox behavior due to the availability of multiple electron vacant sites in the structure. The concentration of metal present in the catalyst was determined by ICP as represented in Table 2. About 50% destruction of nitrosamine was obtained for Pd-OMS-2, which remained almost constant for 4 cycles, whereas Ni-OMS-2 catalyst showed about 58% conversion in the first cycle and dropped to 34% in the fourth cycle. The low activity of nickel could be due to the low nickel concentration in the catalyst. For Ni catalyst, actual concentration obtained by ICP was much lower than theoretical 10 wt% which could be due to the small size of nickel that was unable to fit into the cage structure of OMS-2. The Fe-OMS-2 catalyst was slightly more effective compared to the palladium and nickel based catalysts, with >60% conversion in the first run and stayed at about 55% for the four cycles. This could be due to the presence of enough metal content as represented in Table 2 and fast conversion between Fe^{2+} and Fe^{3+} .

In order to further increase the speed of nitrosamine destruction, the focus was shifted to a mesoporous catalyst design with high surface area. HMS synthesized by a template method generally contains surface area above 500 m²/g (Chen et al., 2013) (Figure 4). The highly ordered structure of silica could provide a narrow pore size distribution and allow uniform metal dispersion and large availability of active sites. It was believed that higher surface area could provide better dispersion of metal and the presence of silica could help to bind nickel tightly. This catalyst was tested for nitrosamine destruction reaction without any characterization. Data obtained from the first cycle does indicate that HMS catalyst is better than that of OMS, but only about 28% conversion of NPy was obtained after the second cycle. Thus Ni-HMS catalyst was

not considered as a suitable catalyst for further studies because of the poor stability of Ni on HMS support.

The design of the catalyst was further directed towards metal loaded over a robust mesoporous support with the strong binding of nickel to increase the catalyst stability. Zirconia based catalyst have been reported for a number of applications due to their high thermal stability and metal binding affinity (Mercera et al., 1990; Sharma and Singh, 2011). For this study, zirconyl oxychloride was converted to zirconium hydroxide by precipitating it with ammonium hydroxide. As presented in Figure 5, the active hydroxide groups present above the plane could possibly bind to metal, providing strong metal-support interaction. As confirmed from XRD, the tetragonal nature was maintained after nickel loading. This catalyst was found to possess excellent activity towards hydrogenation. For the initial 6 cycles, the destruction of 100 mg/L NPy in 5 mol/kg MEA solution was >95% (4 h run time at LHSV of 0.3 h⁻¹).

The Ni-ZrO₂ catalyst was further evaluated to determine its robustness, thermal stability, and capacity for multiple cycles. Under the similar conditions of 120 °C and 120 psi hydrogen pressure (without reactivating or additional makeup), the catalyst was reused for 15 cycles. The catalytic tests resulted in consistent activity of >95% towards destruction of nitrosamines after 4 h for all the cycles (Figure 6). The reaction solution after first and 15th cycle was tested by ICP for dissolved Ni content if any. The analysis showed nickel content in the solvent was below the detection limit (50 ppb) indicating no leaching of metal ions from the catalyst surface.

3.3 Catalyst characterization

The most promising catalyst from the above tests i.e. Ni-ZrO₂, was characterized by SEM, N₂ adsorption-desorption, TPR and XRD techniques. Table 3 collects the results obtained from the

BET and porosimetry determinations that include the BET surface area, pore volume and pore size of the catalysts. Differences have been observed for Ni-ZrO₂ catalyst compared to the ZrO₂ support. The results showed that the BET surface area per gram of the catalyst was reduced with nickel loading probably due to the blockage of pore mouth with nickel oxide. The comparison of the experimental isotherm with the typical IUPAC forms (Uzio, 2001) leads to the conclusion that it is of the type IV with H₁ for ZrO₂ and H₂ for Ni-ZrO₂ hysteresis loop (Figure 7). H₂-type hysteresis is often associated with 'ink-bottle' pores, spheroidal cavities or voids between close-packed spherical particles; on the other hand, H₁-type hysteresis is the characteristic of cylindrical pores. The changes in the loop shape indicate the change in the porous structure of zirconia by loading nickel. Pore size was in the mesoporous range and was reduced from 8.58 for ZrO₂ to 5.54 for Ni-ZrO₂. Values of total pore volume are from adsorption isotherms, which dropped from 0.984 cm³/g for ZrO₂ to 0.185 cm³/g for Ni-ZrO₂.

Surface characteristics of the catalyst were obtained using SEM. Uniform distribution of the particles was observed through the SEM images (Figure 8). Small nickel particles were found deposited on the surface of bulk zirconia. Average particle size was in the mesoporous region.

Figure 9 represents XRD graphs for the catalyst and the support. The peaks obtained were sharper and broader, indicating the crystalline nature of the products. XRD patterns revealed the presence of tetragonal phase of mesoporous zirconia by a sharp peak at 30 ° (Prasad et al., 2011). No peaks that represent monoclinic or cubic zirconia phase were observed. Also, no sharp signal was observed corresponding to NiO at this Ni loading, which indicates that the ZrO₂ structure is not distorted by Ni loading.

TPR studies were performed to determine the reducing ability of the catalyst in the presence of hydrogen gas. Comparisons have been made between TPR data of ZrO₂ and Ni-ZrO₂ catalyst.

From Figure 10 it is clearly seen that blank ZrO_2 does not have any reduction capacity whereas Ni- ZrO_2 catalyst possesses a large number of active sites capable of accepting hydrogen and thus accelerating hydrogenation reaction of NPy.

3.4 Applicability to the mixture of nitrosamines

For a solution in the CO_2 capture process, the concentration of total nitrosamines may involve either one or multiple nitrosamines depending on the solvent under study, and therefore it became important to study the applicability of the method towards destroying multiple nitrosamines together. GC-MS responses were first recorded for each nitrosamine standard sample using NSMO as an internal standard to determine the feasibility of the method used. A mixture of 100 mg/L NPy, 100 mg/L NPz and 200 mg/L NDELA was made in 5 mol/kg MEA solution (Entry 1, Table 4). Similar mixture was made in DI water (Entry 2, Table 4). The solutions were tested at 120 °C and 120 psi hydrogen pressure for 6 h at a LHSV of 0.3 h^{-1} . The total solution concentration of nitrosamine was 400 mg/L, which was four times higher than in the previous experiments (100 mg/L NPy). A higher initial concentration of NDELA and a lower split ratio in the GC method (10:1) was chosen due to its lower GC-MS response. The samples were analyzed without extraction due to high solubility of NDELA in water and its small extraction efficiency. For the solution made in 5 mol/kg MEA, 83, 78 and 46% destruction was observed (Table 4, Entry 1) and for the solution made in water, 86, 82 and 50% destruction was observed (Table 4, Entry 2) for NPy, NPz and NDELA respectively. Thus the synthesized catalyst was found to be suitable for destroying multiple nitrosamines regardless of the solvent matrix. The lower destruction capability of NDELA could be due to its high initial concentration in the solutions or higher relative stability of this compound under the experimental conditions.

4. CONCLUSION

An up-flow reactor was designed to conduct catalytic nitrosamine destruction experiments. Several heterogeneous catalysts were synthesized and evaluated for destruction of NPy in a 5 mol/kg MEA solution. One promising catalyst, Ni-ZrO₂, was tested over 15 cycles providing consistent catalytic activity of >95% destruction. This catalyst was characterized by SEM, XRD, TPR and N₂ adsorption-desorption to determine the surface properties, metallic character and the presence of active sites. Running a mixture of multiple nitrosamines also showed good destruction capacity regardless of the starting material, thus the scope of this method and catalyst was further expanded.

ACKNOWLEDGEMENT

The authors acknowledge the Carbon Management Research Group (CMRG) members, including Duke Energy, Electric Power Research Institute (EPRI), Kentucky Department of Energy Development and Independence (KY-DEDI), Kentucky Power (AEP), and LG&E and KU Energy, for their financial support. The authors would also like to thank Trish Coakley from ERTL-University of Kentucky for assistance during ICP testing. The authors are also thankful to Xin Gao, Yi Zhang and Gary Jacobs for providing assistance in catalyst characterization.

REFERENCES

Aas, N., da Silva, E.F. 2010. Emission measurements at Dong's pilot plant for CO₂ capture in Esbjerg, in Environmental Impacts of Amine Emission During Post Combustion Capture. Oslo, Norway.

311 Cervený L. 1989. Palladium catalysts in hydrogenation reactions. *Chem. Eng. Commun.* 83, 31-
 312 63.

313 Challis, B.C., Challis, J.A. 1982. *N*-nitrosamines and *N*-nitrosimines in *The Chemistry of Amino,*
 314 *Nitroso and Nitro Compounds and their Derivatives*, S. Patai (Eds.), John Wiley and Sons, NY,
 315 2, pp. 1151-1223.

316 a Chandan, P.A., Honchul, S., Harrison, E., Li, J., Thompson, J., Liu K. 2014. Destructing
 317 nitrosamines in post-combustion CO₂ capture. *Energy Procedia*, 63, 808-813.

318 b Chandan P.A., Remias J.E., Liu K. 2014. Possible ways to minimize nitrosation reactions
 319 during post-combustion CO₂ capture process. *Int. J. Greenhouse Gas Contr.*, 31, 61-66.

320 Chandan, P.A., Remias, J.E., Neathery, J.K., Liu, K. 2013. Morpholine nitrosation to better
 321 understand potential solvent based CO₂ capture process reactions. *Environ. Sci. Tech.*, 47,
 322 5481–5487.

323 c Chandan, P.A., Rogers F., Landon J., Remias, J.E., Liu K. 2014. Minimizing solvent
 324 degradation and corrosion using multifunctional additives. *Energy Procedia*, 63, 814-821.

325 Chen, Y.C., Huang, X.C., Luo, Y.L., Chang, Y.C., Hsieh Y.Z., Hsu, H.Y. 2013. Non-metallic
 326 nanomaterials in cancer theranostics: a review of silica- and carbon-based drug delivery systems.
 327 *Sci. Technol. Adv. Mater.* 14, 044407.

328 Dai, N., Shah, A.D., Hu, L., Plewa, M.J., McKague, B., Mitch, W.A. 2012. Measurement of
 329 nitrosamine and nitramine formation from NO_x reactions with amines during amine-Based

330 carbon dioxide capture for post-combustion carbon sequestration, *Environ. Sci. Technol.* 46,
331 9793–9801.

332 da Silva, E.F., Kolderup, H., Goetheer, E., Hjarbo, K.W., Huizinga, A., Khakharia, P., Tuinman,
333 I., Mejdell, T., Zahlsen, K., Vernstad, K., Hyldbakk, A., Holten, T., Kvamsdal, H.M., Os, P.V.,
334 Einbu, A. 2013. Emission studies from CO₂ capture pilot plant. *Energy Procedia.* 37, 778-783.

335 Fine, N. A., Rochelle, G. T. 2013. Thermal decomposition of n-nitrosopiperazine. *Energy*
336 *Procedia.* 37, 1678-1686.

337 Fostas, B., Gangstad, A., Nenseter, B., Pedersen, S., Sjøvoll, M., Sørensen, A.L. 2011. Effects of
338 NO_x in the flue gas degradation of MEA. *Energy Procedia.* 4, 1566–1573.

339 Fridman, A.L., Mukhametshin, F.M., Novikov, S.S. 1971. Advances in the chemistry of aliphatic
340 N-nitrosamines. *Russ. Chem. Rev. Eng. Transl.*, 40, 34.

341 Gangolli, S.D. Shilling, W.H. Lloyd, A. G. 1974. A method for the destruction of nitrosamines in
342 solution. *Food Cosmet. Toxicol.* 12, 168.

343 Graff, O.F. Emission, measurement and analysis from mobile carbon capture test facility, in
344 Environmental Impacts of Amine Emission During Post Combustion Capture. 2010: Oslo,
345 Norway.

346 Knuutila, H., Svendsen, H.F., Asif, N. 2013. Destruction of nitrosoamines with UV-light, *Energy*
347 *Procedia.* 37, 743–750

348 Magee, P.N., Montessano, R., Preussman, R. 1976. *N*-Nitroso compounds and related
 349 carcinogens, in C. E. Searle, "Chemical Carcinogens" (ACS Monograph 173), *The American*
 350 *Chem. Soc.* 491-625.

351 Mercera, P.D.L., Van Ommen, J.G., Doesburg, E.B.M., Burggraaf, A.J., Ross, J.R.H. 1990.
 352 Zirconia as a support for catalysts: Evolution of the texture and structure on calcination in air.
 353 *Applied Catal.* 57, 127-148.

354 Prasad, K., Pinjari, D.V., Pandit, A.B., Mhske, S. T. 2011. Synthesis of zirconium dioxide by
 355 ultrasound assisted precipitation: Effect of calcination temperature. *Ultrason.Sonochem.* 18,
 356 1128–1137.

357 Rochelle, G.T., Ashouripashaki, M., Voice, A.K., Namjoshi, O., Fulk, S. 2013. Thermal
 358 destruction of nitrosamine in CO₂ capture. WO 2013106831 A1.

359 Rochelle, G. T., Chen, E., Dombrowski, K., Sexton, A., Lani, B.
 360 [http://www.netl.doe.gov/File%20Library/events/2013/co2%20capture/G-Rochelle-UTA-](http://www.netl.doe.gov/File%20Library/events/2013/co2%20capture/G-Rochelle-UTA-Concentrated-Piperazine-for-CO2-Capture.pdf)
 361 [Concentrated-Piperazine-for-CO2-Capture.pdf](http://www.netl.doe.gov/File%20Library/events/2013/co2%20capture/G-Rochelle-UTA-Concentrated-Piperazine-for-CO2-Capture.pdf)

362 Shah, A.D., Dai, N., Mitch, W.A. 2013. Application of ultraviolet, ozone, and advanced
 363 oxidation treatments to washwaters to destroy nitrosamines, nitramines, amines, and aldehydes
 364 formed during amine-based carbon capture. *Environ. Sci. Technol.*, 47 (6), 2799–2808.

365 Sharma, Y.C., Singh, B. 2011. Advancements in solid acid catalysts for ecofriendly and
 366 economically viable synthesis of biodiesel. *Biofuels, Bioprod. Bioref.* 5, 69–92.

Strazisar, B.R., Anderson, R.R., White, C.M. 2003. Degradation pathways for monoethanolamine in a CO₂ capture facility. *Energy Fuels*, 17, 1034–1039.

Uzio, D. Textural characterization of catalysts, in: Lynch J. (Editor), *Physico-Chemical Analysis of industrial catalysts*, Edition Technip, Paris, 2001, pp. 5-26.

Yadav, G.D., Chandan, P.A., Nirupama, G. 2012. Green etherification of bioglycerol with 1-phenyl ethanol over supported heteropolyacid. *Clean Techn. Environ. Policy*, 14, 85–95.

Figure 1. Reactor design for lab scale nitrosamine destruction experiments

Figure 2. Contribution by thermal decomposition of nitrosamines at 120 °C and 120 psi pressure

Figure 3. Catalyst evaluation for nitrosamine destruction

Figure 4. Mesoporous silica structure (Chen et al., 2013)

Figure 5. Structure of zirconium hydroxide and zirconia

Figure 6. Stability tests for Ni-ZrO₂ catalyst

Reaction conditions: 100 mg/L NPy in 5 mol/kg MEA, 120°C, 120 psi hydrogen pressure,
LHSV 0.3⁻¹, 4 h

Figure 7. Nitrogen adsorption isotherm of ZrO_2 and Ni-ZrO_2

Figure 8. SEM images of (a) ZrO_2 and (b) Ni-ZrO_2 catalyst

383

Figure 9. XRD for ZrO_2 and Ni-ZrO_2 catalysts

384

Figure 10. TPR data of catalyst indicating the no. of active sites

386

387

Table 1. Detection of nitrosamines by various power plants

388

Plant	Reference	Nitrosamines amount	Location
Maasvlakte (Netherlands)	Da Silva et al., 2013	20 ng/Nm ³ (0.3 ppb) NDELA	Emission
EU project Cesar	Aas and da Silva, 2010	ppb levels	Water wash
Aker Clean Carbon(Norway)	Graff, 2010		
Statoil (Norway)	Shah et al., 2012	0.73 µM for MEA 59 µM for AMP/PZ	
IMC Chemicals Facility (Trona, CA)	Strazisar et al., 2003	2.9 µM for MEA	Amine solution
CO ₂ Technology Centre (Mongstad)	Fostas et al., 2011	5.3 µM NDELA for MEA	
CSIRO (Tarong, Australia)	Rochelle et al., 2013	2.4 mM NitrosoPZ for PZ	

389

390

Table 2. Analysis of OMS-2 catalysts by ICP

Catalysts	%Fe	%Ni	%K	%Mn	%Pd
Fe-OMS	7.05	-	3.09	46.28	-
Ni-OMS	-	2.08	3.9	53.44	-
Pd-OMS	-	-	3.72	48.72	5.89

391

392

393

Table 3. Surface area and pore size distribution of the catalyst

Catalyst	BET surface area (m²/g)	Pore volume (cm³/g)	Absorption Pore size (nm)
ZrO ₂	458.4	0.984	8.58
Ni-ZrO ₂	133.3	0.185	5.54

394

395

#	Solution	% destruction ^a		
		NP _y	NP _z	NDELA
1	In 5 mol/kg MEA	83	78	46
2	In water	86	82	50

396

Table 4. Destruction of nitrosamines in the mixture

397 ^aReaction conditions: 100 mg/L NP_y + 100 mg/L NP_z + 200 mg/L NDELA, 120 °C, 120 psi
 398 hydrogen pressure, Ni-ZrO₂ catalyst 10 g, LHSV 0.3 h⁻¹, 6 h