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Published in:
Environmental Science and Technology

Link to article, DOI:
[10.1021/acs.est.9b03103](https://doi.org/10.1021/acs.est.9b03103)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Santiago, R., Mossin, S., Bedia, J., Fehrmann, R., & Palomar, J. (2019). Methanol Promoted Oxidation of Nitrogen Oxide (NO_x) by Encapsulated Ionic Liquids (ENILs). *Environmental Science and Technology*, 53(20), 11969-11978. <https://doi.org/10.1021/acs.est.9b03103>

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Sustainability Engineering and Green Chemistry

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Environ. Sci. Technol., **Just Accepted Manuscript** • DOI: 10.1021/acs.est.9b03103 • Publication Date (Web): 13 Sep 2019

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Methanol promoted oxidation of NO using Encapsulated Ionic Liquids (ENILs)

338x190mm (96 x 96 DPI)

Methanol Promoted Oxidation of Nitrogen Oxide (NO_x) by Encapsulated Ionic Liquids (ENILs)

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Keywords: NO oxidation; NO_x removal; Ionic Liquids; ENIL; Flue gas

Abstract

The removal of nitrogen oxides (NO_x) has been extensively studied due to their harmful effects to health and environment. In this work, Encapsulated Ionic Liquids (ENILs) are used as catalysts for the NO oxidation at humid conditions and low temperatures. Hollow carbon capsules (C_{Cap}) were first synthesized to contain different amounts of 1-butyl-3-methylimidazolium nitrate IL ([bmim][NO₃]), responsible for the catalytic oxidation. Then, the materials were characterized using different techniques, by analyzing microstructure, porosity, elemental composition and thermal stability. The catalytic performance of ENIL materials was tested for NO conversion at different conditions. Thus, NO concentration was fixed at 2,000 ppm at dry and humid conditions. Then, the methanol promotion of the reaction was demonstrated, increasing the NO conversion values in all cases, and the alcohol/water ratio was optimized. The temperature effect was studied as well, using the optimal conditions based on the previous measurements. The results reflect that humid conditions do not have a negative effect in terms of NO conversion when using ENILs, opposite behavior as the observed for C_{Cap} and traditional catalysts studied before. Low amount of IL inside the material (40% in mass) was found to be the optimum for the task, reaching conversions of almost 45% in near industrial conditions of temperature and O₂ and H₂O concentrations in the flue gas with a GHSV = 10,000 h⁻¹.

Introduction

Nitrogen oxides (NO_x) are one of the major air pollutants from traditional electrical production as fossil fuel combustion, leading to well-known harmful effects ^{1, 2}. These negative effects comprise not only to the human health, causing important respiratory problems ³, but also atmospheric pollution by acid rain, photochemical smog and ozone layer depletion ^{4, 5}. The major constituents of NO_x are nitrogen dioxide (NO_2) and nitric oxide (NO), which is an intermediate of the nitric acid synthesis in the chemical industry. Due to the low solubility of this gas in traditional solvents ⁶, it is attractive to develop systems to remove or convert this compound into value-added or not harmful products. The most important technologies of the chemical industry to remove NO_x present in the flue gas are the well established SCR (selective catalytic reduction) and SNCR (selective non-catalytic reduction) of NO_x ^{7, 8}. However, these methods are not able to remove NO_x completely because of some disadvantages during their use at high operating temperatures ⁹, which also means high costs of the process. The catalysts typically used in SCR, mainly based on V_2O_5 , work at temperatures above 300 °C ¹⁰, taking advantage of the high temperatures of the power plants systems but placed in high dust position, promoting catalyst deactivation. However, other industrial units like waste incineration plants and ships demand also low temperature –end-of-pipe- de- NO_x technologies. Therefore, research efforts have been centered on the development of new catalysts able to eliminate NO at lower temperatures. In this sense, not only the reduction process was taken into account, but others such as catalytic oxidation that was proved to work at lower temperature.

Several works were published in this field using zeolites ¹¹ or carbonaceous materials ¹² in presence of water at low temperature, giving as conclusion that the reaction occurs in the micropores of the material. Recently, an interesting work published by Ghafari *et al.* reports conversions up to 35 % of NO to NO_2 in presence of water by using a polymer based catalyst at near room temperatures ¹³. However, the presence of water decreased the polymer based catalysts performance. For this reason, it is important to develop catalysts are less affected in presence of water, or even with water as promoter to convert NO to value-added products.

Other alternatives to remove NO were also investigated, such as absorption ^{14, 15}. In this case, the absorption capacity of NO in aqueous solutions is reported to be low ¹⁵. For these reasons, big efforts has been tried to enhancing this absorption capacity by means

of using additives¹⁶. Furthermore, it was detected the easy combination of NO with transition metals, so different metals were specifically designed for NO capture¹⁷. All these absorbents were aqueous solutions, limited by the low NO solubility in water¹⁸.

In last years, ionic liquids (ILs) are proposed as new chemical solvents, attracting a huge number of studies in e.g. gas capture applications¹⁹, due to their characteristic properties such as high absorption capacity, low vapor pressure and high thermal and chemical stability²⁰, among others. Therefore, ILs have been extensively evaluated in gas capture, for instance of CO₂²¹, SO₂²², H₂S²³, NH₃²⁴, and volatile organic compounds²⁵. It is remarkable that, however, few works on NO capture by ILs have been reported so far. Chen *et al.*²⁶ reported the first functional IL to capture NO, with the disadvantage of the high difficulty in the synthesis stage. Then, Sun *et al.*²⁷ synthesized a metallic functional ionic liquid able to chemically absorb NO. Recently, Kunov-Kruse *et al.*²⁸ reported that the IL 1-butyl-3-methylimidazolium nitrate ([bmim][NO₃]) is a successful catalyst for NO oxidation into nitric acid in presence of water. However, it is well stated that the practical application of ILs are limited by their unfavorable transport properties^{29,30}. In fact, several efforts have been centered on developing systems and materials able to reduce the kinetic control in the absorption operations based on ILs³¹⁻³³. Thus, Supported Ionic Liquid Phase (SILP) concept was invented³⁴⁻³⁶. It consists of IL deposition in the pores of a solid support (silica, carbon, among others). In the case of gas capture application, these materials increase the mass transport rates compared with pure ILs due to the increase in the gas-liquid interfaces³⁷. In the case of catalysis, it can be used like a solid heterogeneous catalyst for continuous fixed bed reactor systems^{35,38}. Recently, SILPs have been applied to different catalytic reactions. An efficient catalytic system based on metal ligand free in an environmental friendly IL system was successfully developed for Suzuki cross-coupling reactions³⁹. Another metal/IL supported on nano-silica based catalysts were employed in the aldehyde C-H activation showing excellent yields of the desired aryl ketones⁴⁰. Catalysts based on copper-doped silica supporting acidic ILs (based on [HSO₄]⁻ anion) demonstrated a good performance on Biginelly reaction⁴¹. In last years, CO₂ valorization has attracted the attention of the scientific community, using SILPs as catalysts for the reaction of cycloaddition of epoxides^{42,43}. Regarding NO separation, the first approach using SILP materials (silica as support) was successfully applied by Fehrmann's group³³. However, the IL loading can limit the practical application of gas capture³². A more recent alternative has

emerged: the Encapsulated Ionic Liquids (ENILs) concept, in which a high amount of IL (up to 80%) is contained inside hollow carbon capsules (internal diameter of 400-700 nm) with high specific surface area ³¹. The performance of ENIL materials was tested by different gas capture applications such as ammonia ^{31, 44} and CO₂ in both physical ^{30, 45} and chemical ⁴⁶⁻⁴⁸ absorption. These works concluded that the encapsulation of the IL does not decrease absorption capacities and increase very significantly the absorption rates, due to the strong increase of contact surface after IL encapsulation. Furthermore, the nature of the IL does not significantly matter to the gas capture kinetics when using ENIL materials, since it is controlled by carbon capsule morphology [48]. Therefore, ENIL materials are able to solve the kinetic restrictions that pure ILs present in gas capture applications.

At this point, it emerged the idea of taking advantage of the improved mass transfer kinetics of ENIL materials for its application in NO oxidation by ionic liquid catalysis. Therefore, we propose 1-butyl-3-methylimidazolium nitrate ([bmim][NO₃]) for its encapsulation into ENIL materials with different loadings. The IL selection was decided based on the previous work in which it was demonstrated that could be NO oxidized. The aim of this work is to evaluate the performance of a new support (based on hollow carbon capsules) in which the IL is encapsulated forming the ENIL materials in NO catalytic oxidation into NO₂, HNO₂ and HNO₃ in presence of water at low temperatures.

Experimental section

Materials

The IL 1-butyl-3-methylimidazolium nitrate (98 %) was purchased from Iolitec. The reagents used for hollow carbon capsules synthesis: phenol (99 %), paraformaldehyde (95-100 %), aluminum trichloride (95-100 %), ammonia (34 %) and absolute ethanol were supplied by Panreac. In addition, tetraethylorthosilicate (98 %) (TEOS), hexadecyltrimethoxysilane (90 %) (C16TMS) and hydrofluoric acid (48 %) were supplied by Sigma-Aldrich. Nitrogen, air and the mixture containing 10,000 ppmv of NO in nitrogen were supplied by AGA. The methanol (99.8 %) used for the promoted NO oxidation was supplied by Sigma-Aldrich.

ENIL synthesis

The hollow carbon capsules (C_{Cap}) were synthesized as ENIL materials following the procedure reported by Büchel *et al.* ⁴⁹. This methodology has been successfully

applied by our group in the last years ^{46, 48, 50, 51} to obtain the C_{Cap} and then the ENIL materials for their use in gas capture applications. The full description of the procedure can be found in the referred works. In summary, C_{Cap} were synthesized following a “templating” method in which the solid core and the mesoporous shell aluminosilicate (SCMS) were used as template. The colloidal solution was maintained at 30 °C with vigorous stirring to achieve homogenous diameters of the spheres. Then, the shell was grown around the silica core by adding TEOS and C16TMS (to give porosity to the double shell). After being filtrated and calcined at 550 °C, the SCMS was impregnated by a phenolic resin (generated in situ) that will serve as carbon precursor (prior pyrolysis stage). To accomplish this, aluminum trichloride was impregnated in the SCMS as catalyst of the phenolic resin generation. Then, a mixture of paraformaldehyde and phenol was added to completely impregnate the material generating the phenol-paraformaldehyde resin. The resulting material could be heated until 160 °C that is the curing temperature of the resin, during 5 hours and then increased until 850 °C under a nitrogen atmosphere to accomplish the pyrolysis of the material. The resulting carbon was washed with HF in order to remove the remaining silica present, being able to obtain the final hollow carbon capsules (C_{Cap}).

From C_{Cap} , the ENIL materials were prepared using incipient wetness impregnation. 400 mg of C_{Cap} were used and 1 mL of methanol-IL solution was added drop by drop onto the carbon support. Then, the resulting ENIL materials were heated until 85 °C to completely remove the remaining methanol. In this work, four different ILs loadings were tested (20, 40, 60, and 80 % w/w). The complete synthesis process is shown in Scheme 1. The methodology used was applied in several works of our group demonstrating the homogenous distribution of the IL inside the C_{Cap} ^{30, 44, 46-48}.

Scheme 1: ENIL synthesis scheme

ENIL characterization

The C_{Cap} samples were characterized by means of elemental analysis in a LECO CHNS-932 apparatus. The porous structure of the hollow spheres and ENIL materials

156 was also characterized by 77 K N₂ adsorption/desorption using a TriStar II 3020
157 (Micromeritics) equipment after 10 h of degassing at 0.1 mbar and 393 K. The pore size
158 distribution was calculated using t method. The microstructure and morphology of C_{Cap}
159 were studied by transmission electron microscopy (TEM) using a JEOL JEM 2100 HT
160 microscope. Then, the ENIL materials prepared were characterized by means of thermal
161 gravimetric analysis (TGA) and elemental composition to check the amount of IL inside
162 the material before and after reaction using a Mettler Toledo TGA/DSC 1 STARe system.
163 This was carried out under a N₂ flow of 50 mL/min from room temperature until 600 °C
164 with a heating rate of 10 °C/min.

165 *NO oxidation measurements*

166 The prepared ENIL materials and hollow carbon spheres (C_{Cap}) were tested as NO
167 catalysts using a fixed-bed reactor with ENILs volume of approximately 1.2 cm³,
168 corresponding to masses between 0.4-1.0 g depending on the load of IL used. Most
169 experiments were carried out at room temperature (near 24 °C). However, in the
170 experiments in which the temperature was changed, the reactor was placed inside an oven
171 able to control the temperature (regeneration experiments as well). A flue gas was passed
172 through the reactor with a NO concentration of 2,000 ppm. The O₂ content was varied
173 from 6.2 to 16.8 % and balanced with N₂. Three mass flow controllers were used: i)
174 connected to a 1% NO-N₂ bottle; ii) connected to an air bottle; iii) connected to a N₂
175 bottle. The total gas flow for each experiment was set at 200 mL/min. All the reactions
176 were conducted at atmospheric pressure. Furthermore, the top of the reactor was fitted
177 with a three-way valve that allows introducing the gases and the liquid inside the fixed-
178 bed reactor. The flow of the liquid was controlled by a NE-300 Syringe Pump. In this
179 sense, the relative humidity (RH) of the flue gas was changed and studied from 10 to 75
180 % utilizing a syringe filled of deionized water. The addition of the methanol to promote
181 the oxidation reaction was accomplished by adding a water/methanol solution to the
182 system by the Syringe Pump. The methanol concentration (varied from 100 to 1600 ppm)
183 and the flow rate needed were calculated in each experiment in order to maintain the
184 desired conditions. The bottom of the reactor was conducted into a gas cuvette inside a
185 Thermo Scientific Evolution 220 UV-Visible Spectrophotometer. Each measurement
186 collects the whole spectrum from 200 to 600 nm. NO have absorption bands in the ultra-
187 violet (UV) region at 204 nm, 215 nm and 226 nm. This last peak was used to quantify
188 the NO in the exit of the reactor and calculate the conversion. Peakfit.m matlab script was

used for deconvolution of the three peaks, using last one at 226 nm to calculate conversions as a function of the peak area using a standard curve performed with different NO concentrations mixed with an inert gas (N_2). Other peaks that could be identified in the spectra are due to NO_2 having a broad peak around 405 nm and HNO_2 that presents four different peaks from 340 to 390 nm; and the HNO_3 exhibiting a broad peak in the NO region (from 200 to 250 nm). These peaks can indicate which species are being formed depending on the operation conditions tested. In all cases, the conversion was calculated at steady state, i.e. identical spectra obtained during at least 2 hours. Before changing the relative humidity of the inlet gas, the desorption experiment was carried out after heating the sample up to 130 °C using 100 mL/min of N_2 in presence of water (ratio 1:1) to totally remove the water, methanol and nitric acid present in the sample.

Results

C_{Cap} and ENILs characterization

The hollow carbon capsules (C_{Cap}) and the four prepared ENIL materials were characterized by means of microscopy, pore structure, elemental analysis and thermal stability. Thus, Figure 1A shows TEM microscopy image of the C_{Cap} while Figure 1C shows the size distribution of the analyzed sample by several TEM images. Figure 1B presents the N_2 adsorption-desorption isotherm of the C_{Cap} before the incorporation of [bmim][NO_3] IL.

Figure 1: (A) TEM image of the hollow carbon capsules (C_{Cap}) to prepare ENIL materials; (B) N_2 adsorption/desorption isotherms @ 77 K of C_{Cap} and (C) size distribution of C_{Cap}

Figure 1A shows the homogenous size distribution of the material with spherical shape and an external diameter of almost 600 nm with a shell thickness of 200 nm and a large central hole. The N_2 adsorption-desorption isotherm (Figure 1B) is typical of a mesoporous material with a significant microporosity contribution (both as a consequence

of the porosity of the shell). Table 1 reflects the elemental analysis and the summarized information extracted from the N₂ adsorption-desorption isotherms.

Table 1: Carbon capsules (C_{cap}) characterization by means of elemental analysis and N₂ adsorption-desorption @ 77 K.

Characterization technique			
Elemental Analysis		N ₂ adsorption-desorption	
% C (w)	91.40	S _{BET} (m ² /g)	1,494
% H (w)	1.80	V _{micropore} (cm ³ /g)	0.55
% N (w)	0.10	V _{mesopore} (cm ³ /g)	0.68
		Pore size (Å)	41.35

The elemental analysis extracted from Table 1 confirm the carbonaceous nature of the material (more than 90% of carbon). The incorporation of the different amounts of IL in the support is possible due to the high porosity. The material possesses both mesoporosity and microporosity mainly based on the porous shell grown around the central hollow core. Thus, the average pore size is almost 40 Å, which reflects the mesoporosity of the material. In that way, the different amounts of IL can be incorporated in the support filling the double shell first (until 40% of IL) and the large central hole afterwards ³¹. Once the C_{cap} was synthetized and characterized, the ENIL materials can be prepared with different amounts of IL. In order to check the amount of IL incorporated in each sample, Figure 2 shows the TGA analysis of each one.

Figure 2: TGA analysis of the materials used in this work: hollow carbon capsules (C_{cap}) and ENIL materials with four different IL loading (20, 40, 60 and 80 % of [bmim][NO₃]). Analysis carried out with a temperature increase of 10 °C·min⁻¹ under 50 mL·min⁻¹ of N₂.

Starting with the TGA analysis of C_{Cap} , as can be seen in Figure 2, our support is stable at least until 600 °C under nitrogen. Therefore, using this curve as reference, it is possible to estimate the amount of IL present in each sample taking into account the remaining mass at 600 °C (attributed to the carbon support). In all cases, after a little decay prior to 100 °C (possible sorbed water) the final value corresponds perfectly to the nominal amount of each material. The elemental composition results of each material (see Table S1 of Supplementary Information) confirm the conclusions of TGA analysis. In addition, the pore size distribution of all the ENIL materials are shown on Figure S1 of the Supplementary Information confirming almost the same average pore size (40 Å) but decreasing the pore volume by increasing the IL load on ENILs. The experimental N_2 adsorption/desorption isotherms are also included in Figure S2 of Supplementary Information. An increase in the IL loading inside ENIL material leads to the filling of the pores until 60-80%, in which all remained completely occupied or blocked by IL ^{31, 32}.

NO oxidation in dry conditions

The different prepared catalysts were first tested in absence of moisture. Prior to test the ENIL materials performance in NO catalytic oxidation, it is important to understand the behavior of the support (C_{Cap}) under different oxidation conditions. Figure 3 shows the NO conversion in the hollow carbon capsules using different O_2 contents. In this case, the reaction involved in experiments in dry oxygen condition is depicted in Eq. 1.

Figure 3: NO conversion of hollow carbon capsules (C_{cap}) in dry conditions at different oxygen contents. Gas composition: 2,000 ppm NO, 6.3-16.8% O_2 , balance N_2 , Flow: 200 mL·min⁻¹, GHSV=10,000 h⁻¹. Experiments conducted at room temperature.

As can be seen, the trend clearly shows higher catalytic activity by increasing the amount of O₂ in the system, reaching almost 48 % of conversion at 16.8% of O₂. This means that the presence of more O₂ in the system leads to the formation of more NO₂, resulting in higher conversion values (see Figure S3 in Supporting Information). Compared to those previously reported in the literature, we used 10.5% O₂ (almost 40 % NO conversion) which corresponds to those applied at industrial conditions to treat almost 2,000 ppm of NO⁵². Zeolite based catalysts exhibit NO conversions from 5 to 45 %¹¹ depending on the modifications carried out, concluding that those with higher micropore volume show the greatest performance. Zhang *et al.*¹² reported NO conversions up to 57 % using microporous activated carbons. Sousa *et al.*⁵³ used doped carbons reaching conversions up to 75 % in the best case. In view of all these results, our C_{Cap} material, later used as support for ENIL materials, presents NO conversion in dry O₂ conditions in the range of the zeolite catalysts and slightly lower when compared with activated carbons prior to their modification at almost same conditions. These differences may be attributed to the different porous structure of the materials. It is believed and proved that a high microporous structure leads to higher conversions. In the case of our material, it is basically a mesoporous material but presenting high micropore volume (see Table 1). The C_{Cap} performance can be compared with the ENIL catalysts at 10.5% of O₂. In Figure 4,

the NO conversion reached by each material (including the previous discussed C_{Cap}) are compared.

Figure 4: NO conversion of the different materials of the work in dry conditions. Gas composition: 2,000 ppm NO, 10.5% O₂, balance N₂, Flow: 200 mL·min⁻¹, GHSV=10,000 h⁻¹. Experiments conducted at room temperature.

As can be seen, NO conversion decreases by increasing the amount of IL in the catalyst until the conversion remains constant (from 60% IL loading). This could be

explained due to filling of the pores of the C_{Cap} material (see the reduction in BET area while increasing the IL loading in Table S1 of the Supplementary Information). In the case of 20% and 40% ENIL material, the higher conversion may be attributed to partly filled pores exhibiting more efficient IL distribution on the pore surface. From the previous reported data with [bmim][NO₃] IL²⁸, it seems that the presence of water is key leading to the formation of more [NO₃]⁻ anions (anion part of the IL) that may improve the NO removal.

NO oxidation in wet gas

In order to simulate near industrial conditions the catalytic performance of our materials was investigated in gas streams that contain around 10% O₂ and water. Experiments in wet conditions follow the reaction of Eq. 2. More details about the mechanism of NO oxidation reaction in presence of water using [bmim][NO₃] can be found in previous works^{28, 54}.

Figure 5: NO conversion of (A) the hollow carbon capsules (C_{cap}) and (B) the 40 % [bmim][NO₃] ENIL material in different dry and wet conditions (from 10 to 75% Relative Humidity). Gas composition: 2,000 ppm NO, 10.5% O₂, balance N₂, Flow: 200 mL·min⁻¹, GHSV=10,000 h⁻¹. Experiments conducted at room temperature.

Figure 5A clearly shows the catalytic inhibition when water was added into the system employing C_{Cap} as catalyst. NO conversion reaches only a value of 13% at 75% RH. This may be explained by the decrease of the NO adsorption mainly caused by the competitive water adsorption. Some works reported that water affects negatively the NO oxidation using activated carbons (AC) or zeolites. They reached the same conclusion: the NO oxidation inhibition in presence of water is caused by adsorption competition.

Thus, Mochida *et al.*⁵⁵ showed a huge decrease in conversion by increasing RH in AC catalysts. Another work by Mochida *et al.*⁵⁶ showed the limitation of RH > 60% to the NO oxidation using AC catalysts. Guo *et al.*⁵⁷ reported the complete stop in NO oxidation when RH is higher than 20% using AC catalysts. The moisture influence was also studied in zeolite based catalysts⁵⁸ reaching conversions of only 10% when 8% of H₂O is present in the flue gas stream, showing a dramatic inhibiting effect in that kind of catalysts. The most recent study at wet conditions concerns a new polymer based catalyst¹³ in which the inhibition was also demonstrated when 50% RH was employed. In addition, we believe that the inhibition may also be caused by means of *capillary condensation*, described by the Kelvin equation⁵⁹. At the pore diameter of C_{Cap} (about 41 Å, see Table 1), *capillary condensation* at room temperature is expected to occur at a RH around 50-60%⁶⁰ and may thus cause the observed deactivation in Figure 5A for RH > 50%. This phenomenon definitely does not occur when the IL is completely filling the pores of the support. As can be seen, the presence of water does not inhibit the NO oxidation when using ENIL material. This may be explained by the different NO oxidation mechanism by the [bmim][NO₃] catalyst in presence of water that leads to conversion to HNO₃ instead of NO₂ in the dry gas as concluded in the previous work²⁸. A slight increase in the HNO₃ and decrease in the NO₂ regions of the UV-Vis spectrum (see Figure S2 in Supporting Information) was thus found by adding water to the system compared to the C_{Cap} catalyst. Therefore, this IL catalyst the first reported NO oxidation catalyst that is not negatively affected by presence of water.

Figure 6 shows the NO conversion of the studied materials at two different gas humidity levels.

Figure 6: NO conversion of the different materials at two different wet conditions (10 and 50% Relative Humidity). Gas composition: 2,000 ppm NO, 10.5% O₂, balance N₂, Flow: 200 mL·min⁻¹, GHSV=10,000 h⁻¹. Experiments conducted at room temperature.

For 10% RH, it can be seen that the C_{Cap} material exhibits the highest conversion compared to the ENILs. It seems therefore the water levels are not enough for the ENIL materials to exhibit a decreased performance. The conversion follows almost the same trend as observed for the dry experiments, i.e. the NO conversion decreases while increasing the amount of IL in the material until 60% loading above, which it remains constant. However, a closer look reveals that the presence of water in the gas for the 20% ENIL catalyst seems to be partially inhibited compared to dry conditions, as in the case for the C_{Cap}. This may mean that there are still some pores not completely filled with the IL.

Analyzing the 50% RH exposure, the presence of available pores for NO oxidation in the case of 20% ENIL material seems obvious due to the observed reduction in the NO conversion (but to a lesser extent than for C_{Cap}) when compared with 10% RH exposure. This behavior was also concluded in terms of available pores while increasing the amount of ILs in the support by Lemus *et al.*^{31, 32}. The rest of the materials exhibit unaltered behavior, since their activities are not affected by the addition of more water. If we now compare the performance of the materials at 50% RH, it can be seen that the 40% ENIL exhibits slightly higher NO conversion than C_{Cap}, probably due to the difference in mechanism, while the 20% ENIL material shows almost the same behavior as C_{Cap}, followed closely by the other two ENILs. Thus, it can be concluded that flue gas streams that contain high amount of water does not affect the ENIL materials performance (in terms of NO conversion), in contrast to the typical carbon materials (C_{Cap}), in which the reaction is strongly inhibited.

Methanol promoted NO oxidation in wet gas

In the 1990's, methanol promoted NO oxidation at high temperatures (from 700 °C up to 1,000 °C) was investigated^{61, 62}. An increase in terms of NO conversion was reported when methanol was added to the system. Zamansky *et al.* proposed⁶² the addition of a MeOH/H₂O₂ mixture to further increase the catalytic performance. No more work related to the methanol promoted NO oxidation has been published as far as we know. Then, research efforts moved to methanol oxidation in presence of NO. Thus, some papers⁶³⁻⁶⁵ showed an increase in the MeOH conversion in presence of NO (temperatures

from 600 up to 1,200 °C). Furthermore, they proposed a possible mechanism of the oxidation reaction, concluding that radical formation in presence of NO was occurring. Since methanol promotes the NO oxidation, we screened different methanol concentrations to examine our catalysts performance. As far as we know, this is the first work in which this methodology is applied at room temperature using IL-based catalysts. Thus, Figure 7 shows the NO conversion as a function of the RH and the methanol concentration for the 40% ENIL material.

Figure 7: NO conversion in 40% [bmim][NO₃] ENIL material with relative humidity of 10 and 50% and different concentrations of MeOH in the gas phase. Gas composition: 2,000 ppm NO, 10.5% O₂, balance N₂, Flow: 200 mL·min⁻¹, GHSV=10,000 h⁻¹. Experiments conducted at room temperature.

From Figure 7, it can be seen how the NO conversion increases by increasing the methanol concentration until reaching a maximum. That maximum depends on the RH studied but it is located at a MeOH/NO ratio between 0.2-0.4 depending on the RH. Starting with 10% RH, it is clearly seen that NO conversion increases while increasing the amount of methanol until 400 ppm of MeOH whereafter it remains constant up to 1,600 ppm of MeOH. For 50% RH, the same trend is observed but the maximum is reached at 800 ppm of MeOH. It seems that for 50% RH, the NO conversion is higher than at 10% RH at methanol concentrations above 800 ppm. This interesting difference in the trends might be explained by increased HNO₃ formation when more water is present in the system (see figure S4 of the Supporting Information). An interesting work by Xiao *et al.*⁶⁶ studying the mechanism of the methanol oxidation in presence of NO (room temperature performed as well) indicated that NO₂ may play a role in the methanol oxidation. They proposed a series of intermediate reactions involved in the MeOH

387 oxidation when NO₂ is present. In this context, we believe that two of the proposed
388 reactions may be occurring in our system:

391 Reactions (3) and (4) may be occurring in our system due to the observed nitrous
392 acid (HONO) and the absence of NO₂ in the UV-Vis spectrum (see Figure S5 in
393 Supporting Information), not only while adding the first droplets but also at the steady
394 state (especially when high conversions were found). This was immediately found when
395 methanol was added to the system. Furthermore, huge amounts of HNO₃ were detected
396 while adding MeOH to the system (see Figure S5 in Supporting Information), this may
397 be explained by the proposed mechanism by Kunov-Kruse *et al.*²⁸ when using
398 [bmim][NO₃] as catalyst in which HNO₃ was formed in the catalytic reaction in presence
399 of water. In addition, the presence of HONO may lead to fast formation of HNO₃ (due to
400 nitrous acids well-known instability). Therefore, promoted oxidation of NO in presence
401 of MeOH may be explained by radical formation in both the liquid and the gas phase.
402 Low amounts of MeOH that remain absorbed on the IL are simply removed by heating
403 up the sample to 130 °C. This compound can be easily separated from the others involved
404 in the reaction due to the high differences in their volatilities. Future works will be
405 centered on the study of the mechanism of reaction, getting attention the possible other
406 value-added products formed during the reaction.

407 Based on the optimized MeOH addition, two different concentrations for each RH
408 (200 and 400 ppm for 10% RH and 400 and 800 ppm for 50% RH) respectively were
409 selected for testing the different materials.

410

411 Figure 8: NO conversion of the different materials at relative humidity of (A) 10% RH
412 and (B) 50% RH and two different concentrations of MeOH in the gas phase. Gas
413 composition: 2,000 ppm NO, 10.5% O₂, balance N₂, Flow: 200 mL·min⁻¹,
414 GHSV=10,000 h⁻¹. Experiments conducted at room temperature.

415 In

416 Figure 8A, the methanol promoted NO conversions of the different materials at 10%
417 RH can be analyzed. In general terms, all the materials exhibit greater conversions with
418 the addition of MeOH when compared to the same moisture conditions without MeOH.
419 For 200 ppm methanol, it can be seen that the 20% ENIL material presents the highest
420 NO conversions while it seems that the amount of MeOH added is not enough for
421 overcoming the inhibition in C_{Cap} material pores. However, when increasing to 400 ppm
422 of MeOH, the hollow carbon capsules exhibit the highest activity. The measurements
423 show in general that the addition of methanol promotes the reaction at wet conditions
424 independent of the catalyst used.

425

426 Figure 8B shows that the 20% and 40% ENIL materials present the highest
427 conversion at 50% RH, even higher than hollow carbon capsules. This suggests that at
428 high concentrations of water, the presence of MeOH is not compensating for the
429 inhibition of the NO reaction in the C_{Cap} material probably due to pore condensation of
430 water. The results confirm that for wet conditions with addition of methanol, the ENIL
431 materials exhibit a positive effect regarding the NO removal (increase of more than 50%
432 in NO conversion when compared to the same moisture conditions without methanol -
433 Figure 6).

It is important to remark that after testing the performance of each material, TGA analysis was performed to check the amount of IL that remains in the support (see Figure S6 in Supporting Information) after adding water and methanol to the system. In all cases, it was obtained that the same initial amount of IL remained inside the support compared to before the catalytic tests.

Table 2: NO oxidation performance of different catalysts for dry and wet conditions

Catalyst	NO dry conversion (%)	NO wet conversion (%)	Ref.
Active carbon	69	0	57
Active carbon	94	0	57
Active carbon nanofibers	73	18	55
Active carbon nanofibers	64	16	55
Active carbon fibers	89	15	56
Porous polymers	43	35	13
Porous polymers	48	31	13

Table 2 summarizes NO conversion results previously reported in the literature in dry and wet conditions. The experimental conditions are close to those used in our work. As shown, catalysts based on active carbon present a practically complete inhibition when water is added to the system. On the contrary, catalysts based on porous polymers were reported as first materials able to oxidize NO in wet conditions, reaching a NO conversion of 35%. The difference between ENIL materials and those previously reported is that they are not inhibited when water is present in the system, obtaining almost the same NO conversion independently of the amount of water. In fact, 40% NO conversion is the maximum reached for 20% ENIL catalysts in wet conditions. Therefore, it can be concluded that ENIL materials may be an alternative for catalysts typically studied on the literature.

Temperature effect on NO conversion

Previous studies reported an increased NO conversion when decreasing the temperature (a negative apparent activation energy)^{67, 68}, in good agreement with homogenous phase oxidation⁶⁷. Figure 9 shows the NO conversion as a function of the temperature for the C_{Cap} material and the ENIL materials at 50% RH and 800 ppm of MeOH.

Figure 9: NO conversions in (A) hollow carbon capsules (C_{cap}) and (B) ENIL materials as a function of the temperature using 50% Relative Humidity and 800 ppm of MeOH in the gas phase. Gas composition: 2,000 ppm NO, 10.5% O_2 , balance N_2 , Flow: 200 mL·min⁻¹, GHSV=10,000 h⁻¹.

As shown in Figure 9A, the C_{cap} material optimum was found at 45 °C while in the case of the ENIL material (Figure 9B), the maximum is located at 60 °C. In the case of the ENIL material, the maximum at 60 °C may be attributed to the competing limitations (radical formation) at low temperature and the lower gas solubility in the IL at higher temperatures. These conclusions concern the 20 and 40% ENIL materials in which most of the IL seems to be accessible to the gas, contrary to the 60 and 80% ENILs, where the temperature does not affect the NO conversion. The different temperature effect observed on C_{cap} and ENIL materials may be caused by the place in which the reaction is occurring, i.e pores of C_{cap} and IL of ENIL materials. Moreover, it may be easier to retain the absorbed gas on the liquid media than on pores of solid material when temperature is increased. However, in general, the impact of the temperature on the NO conversion is not very important, reaching about 25% at maximum.

It can be concluded that the oxidation at higher temperatures (approaching flue gas stack temperatures) results in a slight increment of NO conversion, i.e. at temperatures close to 60 °C, the NO conversion is in the range of 45%, in presence of water in the gas phase.

Figure 10: Stability measurements using 20% ENIL material using 50% Relative Humidity and 800 ppm of MeOH in the gas phase. Gas composition: 2,000 ppm NO, 10.5% O₂, balance N₂, Flow: 200 mL·min⁻¹, GHSV=10,000 h⁻¹.

Figure 10 presents the stability measurements of 20% ENIL material in four different cycles. As can be seen, NO conversion is maintained for 24 hours. Then, it started to decrease due to the IL saturation by NO_x and HNO₃ formed. The increase in the temperature up to 130 °C allows the complete regeneration of the catalyst reaching the same values of the fresh one. Therefore, it was demonstrated one day stability and the easy regeneration of the catalyst by a simple temperature increase.

Encapsulated Ionic Liquids (ENILs) were successfully applied as catalysts for NO oxidation at low temperatures. ENILs with different loads of the IL [bmim][NO₃] were synthesized and then characterized by means of elemental analysis, thermal stability, porous structure and microscopy. Experiments in dry gas show higher NO conversion of the hollow carbon capsules compared to ENILs, where the conversion increased with decreasing the IL loading. Experiments conducted at different relative humidities showed positive effect on NO conversion for the ENIL materials. On the contrary, the results of empty carbon material showed inhibition of the NO oxidation by increasing humidity in the system. The reaction was promoted (in presence of water) by addition of methanol to the system. The amount of methanol added to the system was optimized (at different RH), showing an optimal MeOH/NO ratio between 0.2-0.4. In this case, ENILs composed of 20 and 40% of IL exhibited the greatest performance (including hollow carbon capsules) reaching conversions near 45%. The temperature effect on the reaction revealed an optimum temperature of 60 °C when using ENILs, accomplishing relative NO conversions 20% higher than at room temperature ones. Stability measurements revealed

NO conversion is maintained during at least 24 h without any loss. The catalyst was easily regenerated by increasing the temperature up to 130 °C. These results demonstrate potential application of ENILs as catalysts at near industrial flue gas conditions to create “fast SCR” for a down-stream traditional SCR catalyst.

Supporting Information: Elemental composition characterization of ENIL materials involved in the work. Pore size distribution of the materials involved in the work. N₂ adsorption/desorption isotherms @ 77 K of all the materials involved in the work. UV-Vis Spectrum of hollow carbon capsules (C_{Cap}) in dry conditions at different oxygen contents. UV-Vis Spectrum of 40% [bmim][NO₃] ENIL material (40% ENIL) in dry and 10% Relative Humidity conditions. UV-Vis Spectrum of 20% [bmim][NO₃] ENIL material (20% ENIL) in 50% Relative Humidity and 800 ppm of MeOH conditions. TGA analysis of the materials used in this work: hollow carbon capsules (C_{Cap}) and ENIL materials with four different IL loads (20, 40, 60 and 80 % of [bmim][NO₃]) after being used in the catalytic reactions.

Acknowledgments

The authors thank the Ministerio de Economía y Competitividad (MINECO) of Spain (project CTQ2017-89441-R) and Comunidad de Madrid (P2018/EMT4348) for financial support. Rubén Santiago also thanks David Nielsen for his great support at DTU.

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Methanol promoted oxidation of NO using Encapsulated Ionic Liquids (ENILs)

84x47mm (96 x 96 DPI)