Catalytic wet air oxidation of aniline on transition metal modified MCM-41 catalysts

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Abstract

Transition metal (Cu, Cr and V) MCM-41 catalysts were prepared hydrothermally and characterized by X-ray diffraction (XRD), scanning electron microscopy/energy dispersive X-ray (SEM/EDX), inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and N_2 adsorption-desorption analysis at -196ºC. The catalysts were tested in the catalytic wet air oxidation (CWAO) of aniline aqueous solutions at 200ºC and 6.9 bar of oxygen partial pressure. The (Cu)MCM-41 catalyst showed the best performance with respect to combined activity and selectivity for aniline conversion to non-organic compounds. After 2 h of reaction, 96% aniline conversion and 76% of selectivity were attained. Under the employed reaction conditions, leaching of copper was detected in small extent. However, heterogeneous catalytic activity was proved and attributed to copper oxide anchored to MCM-41.

1 Introduction

Recently, the discovery of mesoporous molecular sieves (in particular hexagonal MCM-41) attracted great interest from both fundamental and applied standpoints. They possess tailored pore size with well defined hexagonal mesopores in a simple geometry, leading to reproducible surface properties. Hence, MCM-41 based materials are targeted for their potential applications as heterogeneous catalysts, catalyst supports, molecular hosts and adsorbents (Selvam et al., 2001). Various MCM-41 based materials with hetero metal ions have been synthesized, characterized and extensively tested as catalysts (Ziolek, 2004). Following our previous experience in CWAO (Gomes et al., 2004, 2005), these materials called our attention as potentially useful in this kind of reactions. In the present work, we produced transition metal (Cr, Cu and V) MCM-41 based catalysts and tested them in the CWAO of aniline.

CWAO is a process for oxidative treatment of industrial wastewaters, known by its high efficiency in eliminating chemical oxygen demanding species, by means of an oxidizing source (oxygen or air) under relatively mild conditions (125-220ºC, 5-50 bar), in the presence of a suitable catalyst.

Aniline was chosen as a model compound because is a highly toxic and carcinogenic compound, often present in industrial wastewaters, including those from the textile, rubber production and agrochemical plants. US Environmental Protection Agency (EPA) considers aniline to be a probable human carcinogen and a concentration as low as 600 μg/L in water sources is referred as having high probability of developing cancer upon water ingestion.

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2 Experimental

The catalysts were synthesized hydrothermally as per the procedure outlined elsewhere (Sakthivel and Selvam, 2002; Dapurkar and Selvam, 2005). They have a Si/M (M = Cr, Cu or V) molar ratio of 50. All the samples were characterized by XRD (Rigaku), SEM/EDX (JEOL JSM-6301 F), ICP-AES (Labtam Plasma 8440) and N_2 adsorption-desorption analysis at -196ºC. The surface area was estimated using the Brunauer-Joyner-Halenda (BJH) method. The pore volume was determined from the amount of N_2 adsorbed at $P/P_0 = 0.5$.

CWAO experiments were performed in a 160 mL, 316 stainless steel high pressure reactor (model 4564, Parr Instrument Co.), equipped with a magnetically driven stirrer and a thermocouple. The reactor was heated by an electrical heating mantle controlled by a temperature control unit (model PID 4842, Parr Instrument Co.). Typically, in an oxidation run, the reactor was loaded with a 2g/L aniline solution and 10.7g/L of catalyst (for CWAO runs), which was further heated to the desired reaction temperature. Once the set temperature was achieved, the first sample was withdrawn. After pressurization with air, time zero of reaction was considered. Periodically, 1 mL of liquid sample was collected from the reactor to be further analyzed. At the end of the reactions performed with (Cu)MCM-41, the catalysts were recovered by filtration for reutilization studies and the filtrates analyzed by atomic absorption (Varian Spectra AA 220) for copper leaching evaluation.

Aniline concentration was analyzed by gas chromatography on a capillary column (WCOT fused silica 30 m, 0.32 mm i.d., 1 μm film). The samples TOC content was determined with a Shimadzu TOC analyzer. Total carbon (TC) was measured first, followed by inorganic carbon (IC) measurement. The TOC was calculated subtracting IC from TC. With the experimental values of aniline concentration and TOC it is possible to calculate the reaction selectivity to non-organic compounds (S_{NOC}), defined as $100\times(X_{TOC}/X_{Aniline})$, where X_{TOC} and $X_{Aniline}$ are TOC and aniline conversions, respectively.

3 Results and Discussion

The characterization of the prepared catalysts is summarized in Table 1.

Table 1 – Characterization (XRD, ICP-AES and N_2 adsorption-desorption analysis at -196ºC) of the MCM-41 based materials

Catalyst	Crystal radii (Å)	Average unit cell, a_0 (Å)	Metal content (wt %)	Pore volume (cm^3g^{-1})	Pore diameter (Å)	Surface area (m^2g^{-1})
MCM-41	0.40	43.56	—	0.80	30	1080
VMCM-41	0.50	46.94	0.76	0.83	29	919
(Cr)MCM-41	0.76	43.52	1.23	0.81	27	989
(Cu)MCM-41						
Before reaction	0.71	43.60	1.10	0.75	28	980
After reaction	0.71	42.49	0.90	0.68	24	894

From XRD data, the average unit cell parameter, a_0, of each catalyst was calculated. It is observed that the a_0 values for MCM-41 containing copper and chromium samples (43.56 ± 0.04 Å), are the very same value as found for the MCM-41 siliceous material. This is a strong indication that copper and chromium ions do not substitute in the matrix but are present as extra framework species. In general, the incorporation of a larger cation, such as Cr^{3+} (0.76 Å) or Cu^{2+} (0.71 Å), in tetrahedral geometry for Si^{4+} (0.40 Å) is expected to increase to a significant extent the a_0 parameter value. SEM observations of (Cu)MCM-41 indicate that copper is also present as non-framework (copper oxide) species on the solid external surface of MCM-41 (Figure 1), as concluded by local EDX analysis, in addition to the extra-framework (anchored and dispersed) copper species on the pore walls.

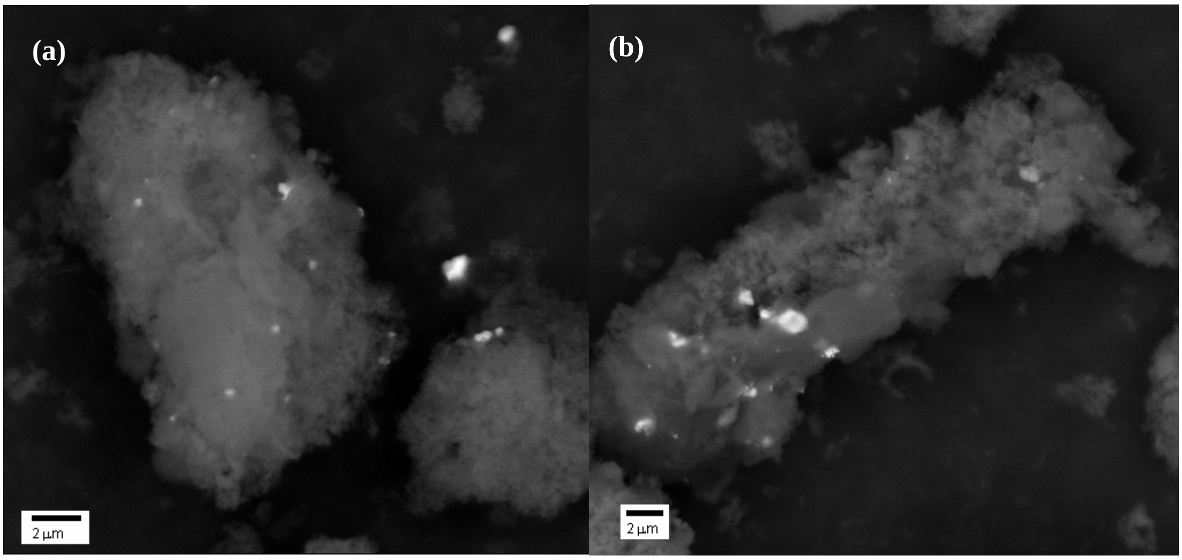

Figure 1 – SEM micrographs of (Cu)MCM-41 catalyst showing the copper distribution over MCM-41: (a) before reaction and (b) after reaction

On the other hand, an increase in the a_0 value was observed for MCM-41 containing vanadium, which could be explained in terms of silicon substitution within the lattice. The increase in a_0 is due to the large ion radius of V^{5+} (0.50 Å) when compared to that of Si^{4+} (0.40 Å) as well as to the V-O bond length (1.8 Å) compared to that of Si-O (1.6 Å), thus supporting the possible substitution of pentavalent vanadium ions in the silicate framework of MCM-41.

The mesoporous nature of the materials was confirmed by determination of their adsorption-desorption isotherms (Figure 2). A sharp inflection between relative pressure P/P_0 = 0.2 and 0.3 corresponds to capillary condensation within uniform mesopores. No defined hysteresis loop in the adsorption and desorption cycle upon pore condensation was obtained, which can be attributed to the uniform size of the particles. The pore volume, surface area and pore diameter calculated from the N_2 adsorption isotherms of all the metal containing MCM-41 samples are given in Table 1.

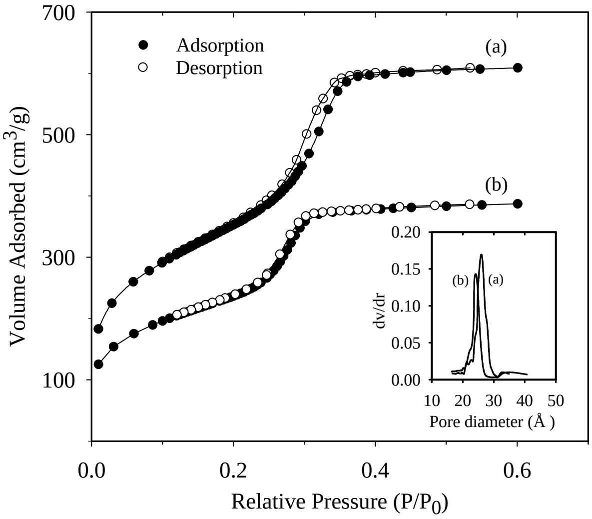

Figure 2 – Nitrogen adsorption-desorption isotherms of (Cu)MCM-41: (a) before reaction and (b) after reaction. Inset shows the pore size distribution.

The different catalysts were tested in the CWAO of aqueous solutions of aniline at 200ºC and 6.9 bar of oxygen partial pressure. The concentration curves are given in Figure 3 (the curve in the absence of catalyst is also given for comparison purposes) and the aniline conversion, TOC conversion and selectivity to non-organic compounds formation, after 2 h of reaction, are in Table 2. It is clear that the non catalytic wet air oxidation of aniline is significant, with an aniline conversion of 45.1% being obtained after 2 h. The corresponding TOC conversion is 27.4%, which gives a selectivity to non-organic compounds formation of 60.8%, clearly indicating that other intermediate products are formed. During the experiment, the formation of an orange colour was observed, suggesting that some azo compounds may be produced. The conversions in the presence of VMCM-41 and (Cr)MCM-41 materials are similar to that obtained in the absence of any solid. In practice, we can assume that, in the present conditions, these materials have no catalytic activity towards oxidation of aniline. When (Cu)MCM-41 catalyst was used, aniline conversion increases rapidly as the reaction proceeds, approaching a limiting value well above 90%, already after 60 min, thus evidencing catalytic activity. With this catalyst, a conversion of 96% is obtained after 2 h of reaction. The corresponding TOC removal is 72.9%, which gives a selectivity to non-organic compounds formation of 75.9%.

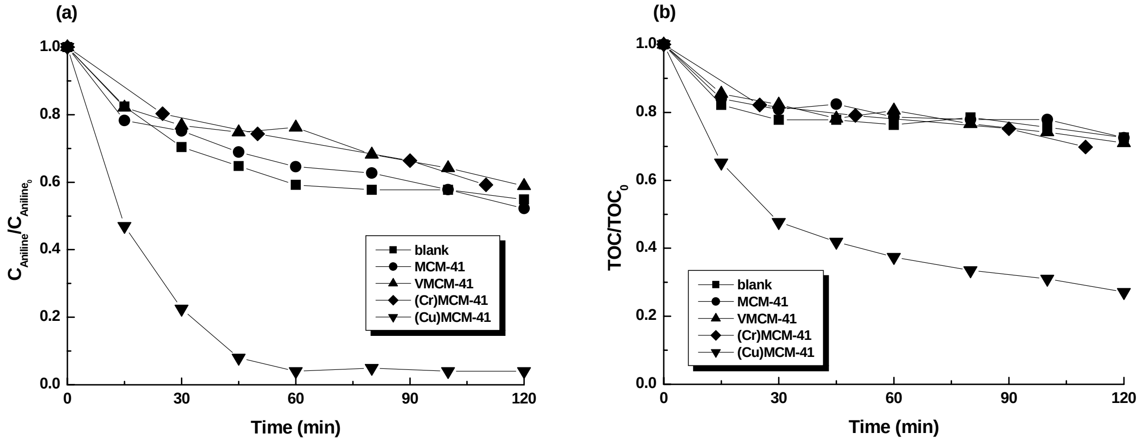

Figure 3 – CWAO of aniline (200ºC and 6.9 bar of oxygen partial pressure) in the absence (blank) and in the presence of MCM-41 alone or modified with several transition metals: (a) aniline concentration curves and (b) TOC concentration curves over 2 hours of reaction.

Table 2 - Reaction data obtained after 2 h for the CWAO of aniline over various catalysts at 200ºC and 6.9 bar of oxygen partial pressure

Catalyst	Conversion (%)	TOC conversion (%)	Selectivity to non-organic compounds (%)
Blank	45.1	27.4	60.8
MCM-41	47.8	27.5	57.5
VMCM-41	41.1	29.0	70.6
(Cr)MCM-41	40.8	30.2	74.0
(Cu)MCM-41			
1st run	96.0	72.9	75.9
2nd run	98.5	82.6	83.9
3rd run	97.1	76.1	78.4
$Cu(NO_3)_2$ + MCM-41	69.9	48.3	69.2

The performance of the (Cu)MCM-41 catalyst was tested by conducting three oxidation runs with the same catalyst after recovering it by filtration, washing with water and drying it in an oven overnight at 110ºC. The obtained results are shown in Figure 4.

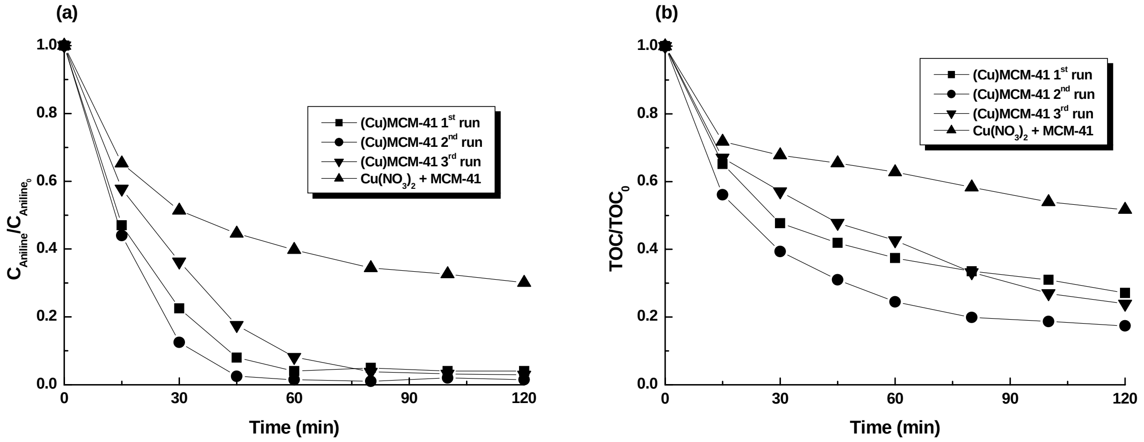

Figure 4 – CWAO of aniline (200ºC and 6.9 bar of oxygen partial pressure). Consecutive runs using (Cu)MCM-41 catalyst and reaction with Cu(NO$_3$)$_2$ + MCM-41 (same copper concentration as copper leached during the first run with (Cu)MCM-41): (a) aniline concentration curves and (b) TOC concentration curves over 2 hours of reaction.

From the analysis of Figure 4 it can be observed that the (Cu)MCM-41 catalyst shows identical profiles in consecutive runs of aniline CWAO. In the second run, the aniline and TOC conversions after 2 h of reaction were 98.5 and 82.6%, respectively, against 96.0 and 72.9% in the first reaction. The corresponding selectivity towards non-organic compounds formation increased from 75.9% in the first run to 83.9% in the second run, mainly as a result of an increase in TOC conversion. In the third run, the aniline and TOC conversions and the selectivity towards non-organic compounds formation (97.1, 76.1 and 78.4%, respectively), had values between those of the previous runs.

It is well known from the literature that homogeneous copper catalysts are very active in the CWAO of several organic compounds. Accordingly, the observed activity obtained with the (Cu)MCM-41 catalyst could be attributed to copper leaching into the solution, causing the occurrence of homogeneous catalysis. Although the catalyst performance was unaffected, leaching of equivalent trace amounts of active copper into solution could happen in all runs (Sheldon et al., 1998). The evaluation of copper leaching was carried out by atomic absorption analysis of the filtered solutions obtained after the reactions and confirmed by ICP-AES analysis of the recovered catalysts. Copper concentrations of 21.6, 22.8 and 28.7 mg/L were detected in the filtrates obtained after the first, the second and the third reaction runs, well below the 121 mg/L reported in a previous work dealing with the CWAO of phenol at 150ºC using (Cu)MCM-41 catalysts prepared by impregnation (Wu et al., 2001). In order to evaluate if the observed activity of (Cu)MCM-41 is all due to the amount of leached copper into solution, a new reaction run was performed using a physical mixture of the homogeneous catalyst Cu(NO$_3$)$_2$ (same copper concentration as leached copper in the first run) and of MCM-41. The results obtained are also given in Figure 4 and in Table 2, allowing direct comparison with the results obtained with the (Cu)MCM-41 catalyst. Analysis of Figure 4 allow to conclude that, although, as expected, the homogeneous catalyst shows a rather good performance (69.9% aniline conversion and 48.3% TOC removal after 2 h of reaction), (Cu)MCM-41 presents heterogeneous catalytic activity. It is also worthwhile noticing that the selectivity to non-organic compounds obtained with (Cu)MCM-41 catalyst (75.9%) is higher than the observed in the homogeneous run (69.2%). The evidence of the reported heterogeneous catalysis and good selectivity gives further support to explore the promising characteristics of hydrothermally synthesized (Cu)MCM-41 catalysts for use in catalytic wet air oxidation reactions. The XRD pattern and BET surface area of the used catalyst showed that the structural integrity of (Cu)MCM-41 is not significantly altered during reaction (Table 1) and the mesoporous nature of the used catalyst was confirmed by nitrogen adorption-desorption measurements (Figure 2).

In the reactions performed either with the (Cu)MCM-41 catalyst, or with the homogeneous $Cu(NO_3)_2$ mixed with MCM-41, traces of a dark brown residue were detected in the solution at the end. EDX analysis of the residue confirms the presence of copper oxide. SEM observations of the used catalyst confirms the same copper distribution pattern observed in the fresh catalyst (Figure 1) and the presence of copper as copper oxide, indicating that copper oxide may be the active state of copper in the aniline oxidation reactions performed with the (Cu)MCM-41 catalyst.

The results here described, show that the (Cu)MCM-41 catalyst is highly efficient for the catalytic wet air oxidation of aniline. The lack of activity concerning Cr and V catalysts is not surprising, especially in the case of Cr, which was already reported to have low reactivity for CWAO reactions when supported over ceria (Barbier Jr. et al., 1998) or even when used as homogeneous catalyst (Imamura, 1999). Although the vanadium catalysts are very promising for selective oxidations at low temperatures, their performance in CWAO reactions, to our knowledge, have not been reported previously. It seems that under the more harsh conditions used for the latter reactions, vanadium shows a complete lack of activity.

4 Conclusions

The (Cu)MCM-41 catalyst prepared hydrothermally showed a very high efficiency for the catalytic wet air oxidation of aniline. After 2 h of reaction, 96.0% aniline conversion and 72.9% TOC reduction were obtained at 200ºC and 6.9 bar of oxygen partial pressure. The selectivity toward non-organic compounds formation was 75.9%. Recycling tests show that the copper catalyst is able to be used again, although copper leaching in small extent was detected. Copper oxide was found to be the active state of copper responsible for the observed (Cu)MCM-41 heterogeneous catalytic activity. These results are quite promising for the application of (Cu)MCM-41 catalysts in the CWAO of aniline containing wastewaters.

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