Synthesis of quinoline derivatives by an improved Döebner-von Miller reaction using a recyclable Ag(I)-exchanged Montmorillonite K10 catalyst

Janeeka Jayram and Vineet Jeena*

School of Chemistry and Physics, University of KwaZulu-Natal, Scottsville, Pietermaritzburg, 3209, South Africa

Email: jeenav1@ukzn.ac.za

Electronic Supplementary Information

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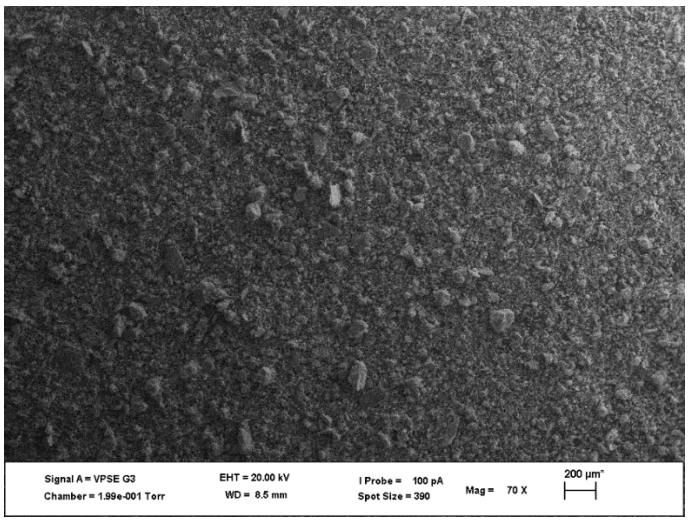
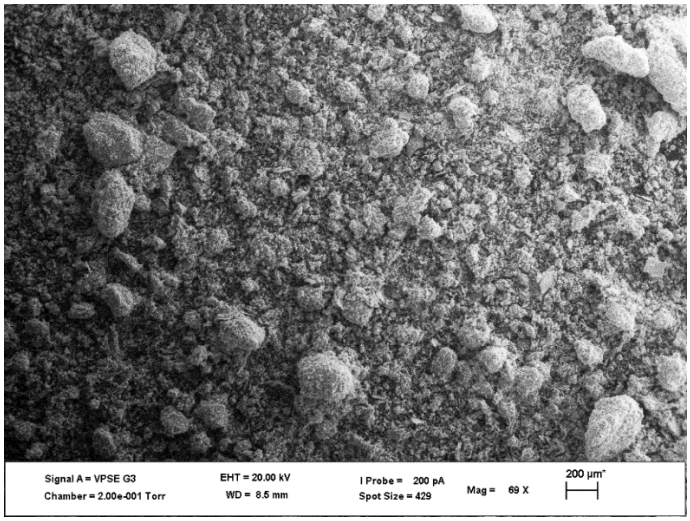
Figure 1: Physical appearance of Montmorillonite K-10 (left) and Ag(I)-exchanged Montmorillonite K-10 (right)

Figure 1 shows the physical appearance of Montmorillonite K10 (left) and Ag(I)-exchanged Montmorillonite K10 (right). Natural Montmorillonite-K10 appears as a dark grey solid and as seen in figure 1, the change in the physical appearance of modified Montmorillonite K10 indicates a change in the chemical composition of the clay. This is confirmed in the SEM and EDX analysis of both catalysts that follow.

The SEM images of Montmorillonite K10 clay and Ag(I)-exchanged Montmorillonite K10 are represented in **Figure 2**. Natural Montmorillonite K10 **(a)** shows some smooth regions in its structure. There is a distinct change in the surface morphology brought about by the addition of silver **(b)**.



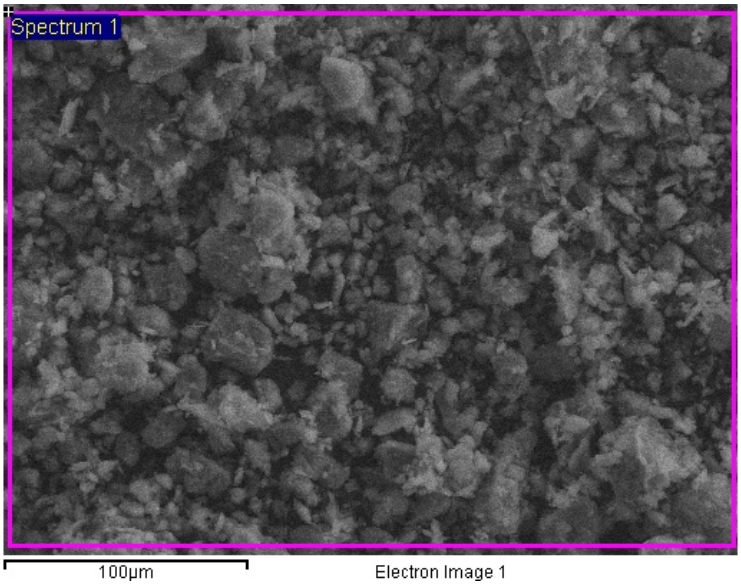
(a)



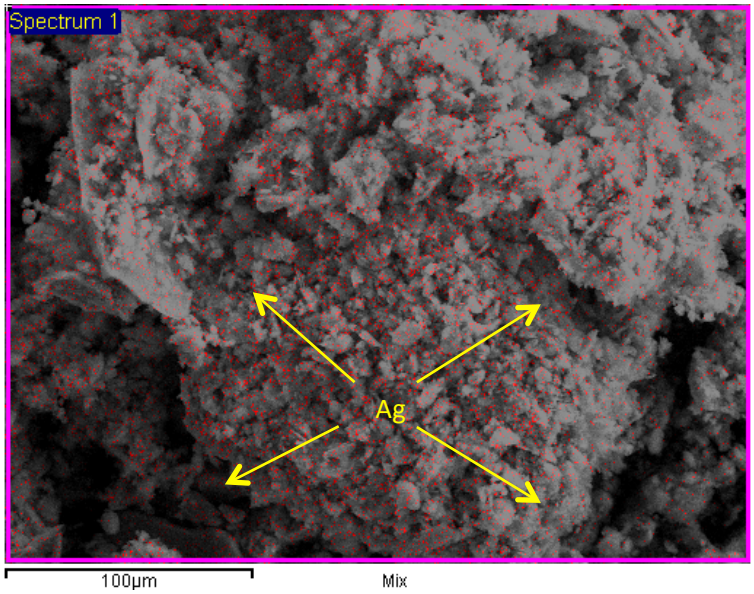
(b)

Figure 2: SEM image of (a) Montmorillonite K10 and (b) Ag(I)-exchanged Montmorillonite K10

The surface of Ag(I)-exchanged Montmorillonite K10 was analyzed by Scanning Electron Microscopy (SEM) for the presence of silver ions and compared to unmodified natural Montmorillonite K10. As can be seen in the data below (**Figure 3**), no silver ions are present in natural Montmorillonite K10 **(a)** while Ag(I)-exchanged Montmorillonite K10 shows a uniform distribution of silver ions as indicated by the pink dots **(b)**.

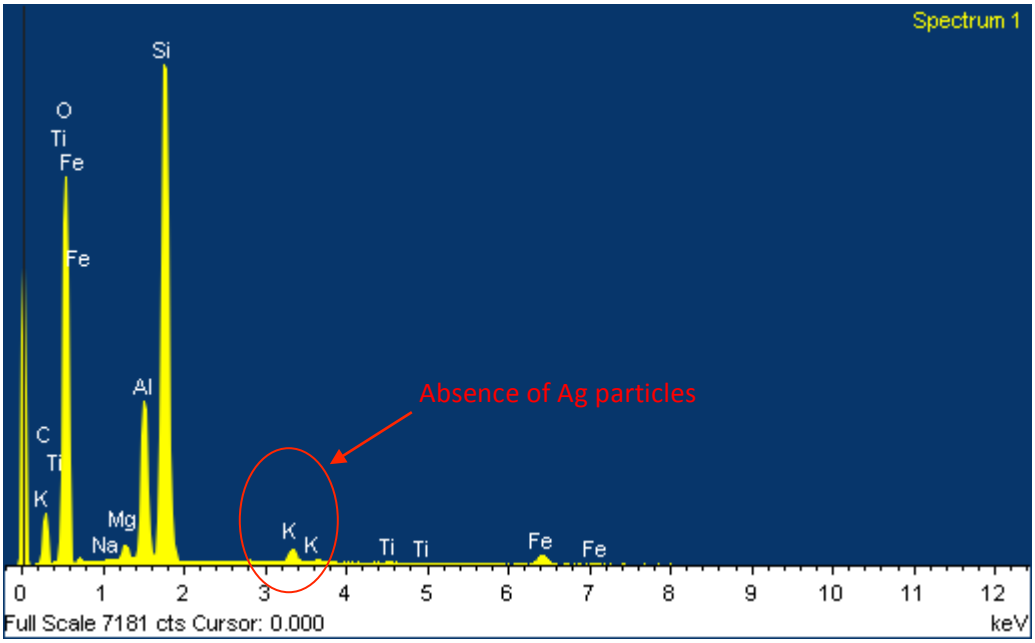


(a): Natural Montmorillonite K10

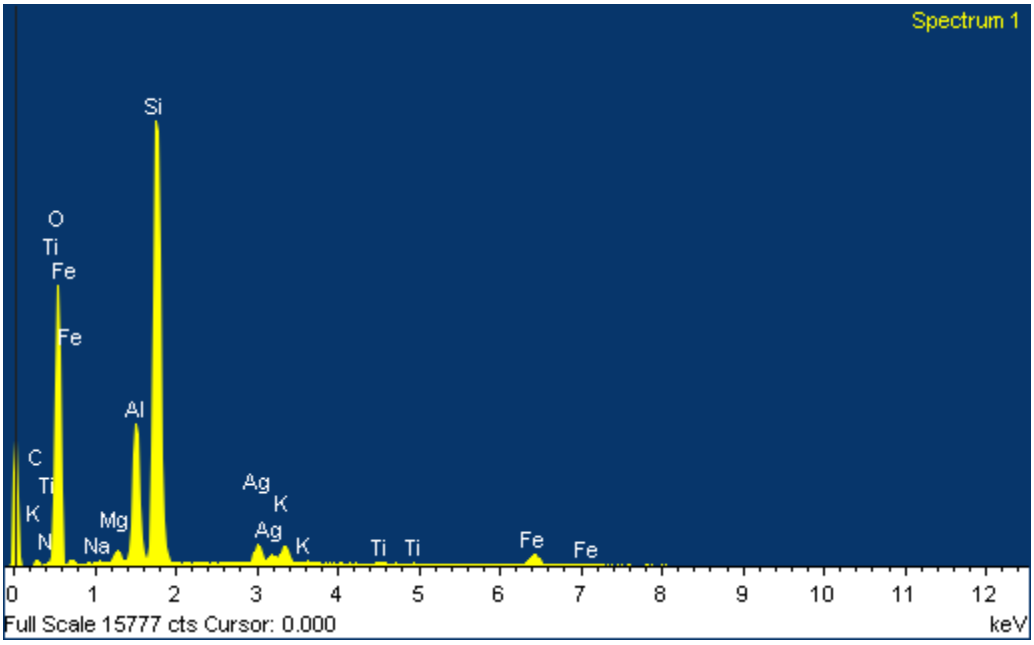


(b): Ag(I)-exchanged Montmorillonite K10

Figure 3: EDX-Mapping showing the **(a)** absence of Ag ion on natural Montmorillonite K10 and **(b)** presence of silver particles on Ag(I)-exchanged Montmorillonite K10



(a)



(b)

Figure 4: EDX spectra of **(a)** Montmorillonite K10 and **(b)** Ag(I)-exchanged Montmorillonite K10

Table 1: Elemental analysis of Montmorillonite K10 and Ag-K10 (major element composition)

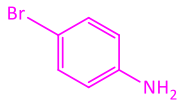
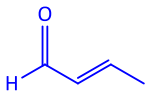
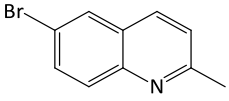
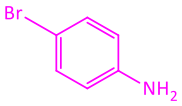
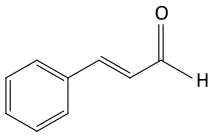
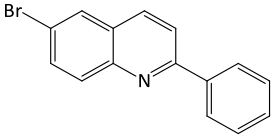
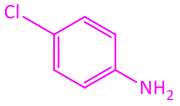
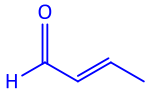
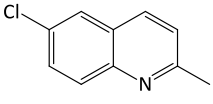
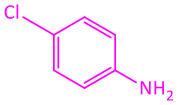
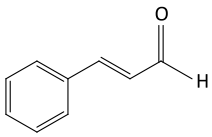
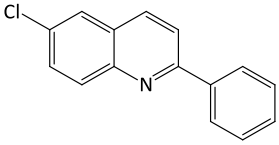
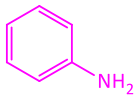
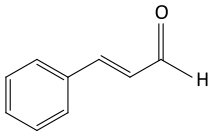
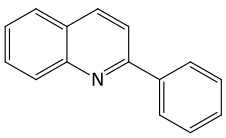
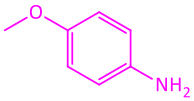
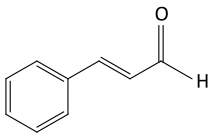
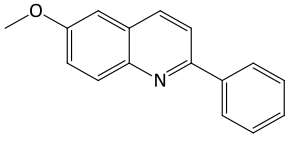
Element (wt%)	O	Na	Mg	Al	Si	K	Ti	Fe	Ag
Montmorrilonite-K10	**52.90**	**0.05**	**0.56**	**5.02**	**17.81**	**0.74**	**0.14**	**1.56**	**-**
Ag(I)-exchanged Montmorillonite K10	**54.33**	**0.13**	**0.72**	**6.85**	**25.22**	**1.25**	**0.30**	**2.77**	**3.67**

The SEM results are also supported by EDX analysis (**Figure 4**). According to figure 4b, it can be seen that silver ions are adsorbed onto natural Montmorillonite K10. Numerical values are given in **Table 1** indicating the main elemental composition. In both cases, the surface composition consists mainly of oxygen, aluminum and silicon and the total silver content, in Ag(I)-exchanged Montmorillonite K10 was found to be 3.67%.

Preparation of Ag(I)-exchanged Montmorillonite K10

Ag(I)-exchanged Montmorillonite K10 catalyst was prepared using an ion-exchange procedure. Silver nitrate (5g) was mixed with distilled water (100 mL) and Montmorillonite K10 (10 g). The mixed suspension was stirred for 4 days at room temperature. The clay was filtered under vacuum and washed with water several times. The resulting powder was dried and subsequently ground to a fine powder to produce the Ag(I)-exchanged montmorillonite K10 catalyst.

Table 1: Comparison study for the synthesis of quinoline derivatives

Amine	α, β-unsaturated aldehyde	Quinoline	Isolated Yield (%)		Reported reaction conditions
			This work	Reported	
			81	16 [1] 86 [2]	10 M HCl/toluene Phosphotungstic acid/toluene
			42	nd [1, 2]	10 M HCl/toluene Phosphotungstic acid/toluene
			80	53 [3] 84 [2]	6 M HCl/$ZnCl_2$ Phosphotungstic acid/toluene
			56	nd [2] nd [3]	Phosphotungstic acid/toluene 6 M HCl/$ZnCl_2$
			89	<1 [1] nd [2]	10 M HCl/toluene Phosphotungstic acid/toluene
			46	<1 [1] nd [2]	10 M HCl/toluene Phosphotungstic acid/toluene

nd = not determined

In order to highlight an improvement in the synthesis of quinoline derivatives using a Ag(I)-exchanged Montmorillonite K10 approach, the yields obtained were compared to literature.

As the data indicates, low to moderate yields are mostly observed under harsh reaction conditions. Moreover, we are able to highlight the scope of our methodology to accommodate both aromatic and aliphatic α, β-unsaturated aldehydes. In a number of literature cases, a limited number of substrates were evaluated and, where no comparison was possible, this was indicated with 'not determined'.

References

1. K. A. Reynolds, D. J. Young and W. A. Loughlin, *Synthesis.*, 2010, **21**, 3645-3648.
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3. C. M. Leir, *J. Org. Chem.*, 1977, **42**, 911-913.