Supplementary Data

This supplementary data is a part of paper entitled "Synthesis and Application of $Fe_3O_4/SiO_2/TiO_2$ Nanocomposite as a Photocatalyst in CO_2 Indirect Reduction to Produce Methanol".

SUPPLEMENTARY (S1)

The product of indirect reduction was analyzed using GC-MS to determine the component of the product. Fig. 1 is the chromatogram of the product and the data summarize in Table 1.

Table 1. Summary of the indirect reduction product

Peak number	Retention time (min)	Peak area (%)	MS prediction
1	1.889	29.65	Formaldehyde
2	1.943	40.66	Methanol
3	1.992	3.59	Formic Acid
4	2.108	26.09	CO_2

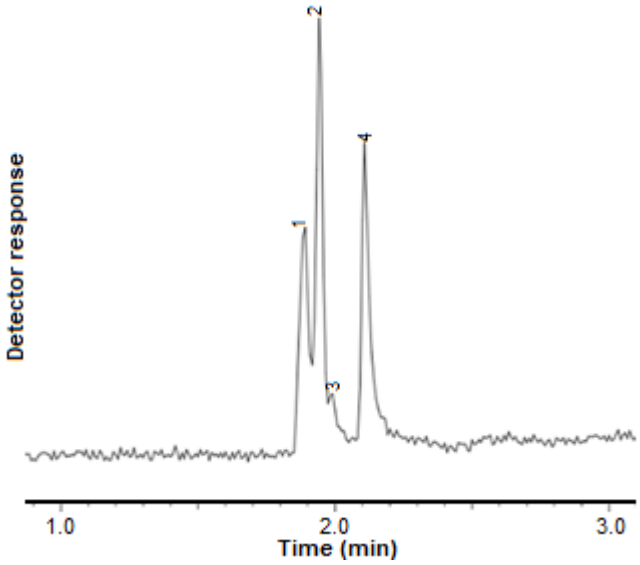

Fig 1. The chromatogram of the indirect reduction product

The retention time of peak 1 is 1.889 min with peak area 29.65%. The compound was analyzed using mass spectrometer and gives mass spectrum in Fig. 2. The spectrum shows that peak 1 has 4 fragments. The fragments with m/z = 30 (molecular ion), m/z = 29 (base line), and m/z = 28 belong to the fragment in formaldehyde fragmentation, shown in Fig. 3. Fragment with m/z = 44 could be fragment from fragmentation of formaldehyde hydrate as shows in Fig. 4. This phenomenon could be occurred because the sample is aqueous solution. The presence of water as solvent gives the chance to formaldehyde to be hydrated. The peak 1 could be interpreted as formaldehyde and it is in agreement with MS prediction.

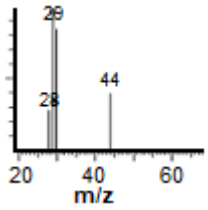

Fig 2. MS spectrum of peak 1

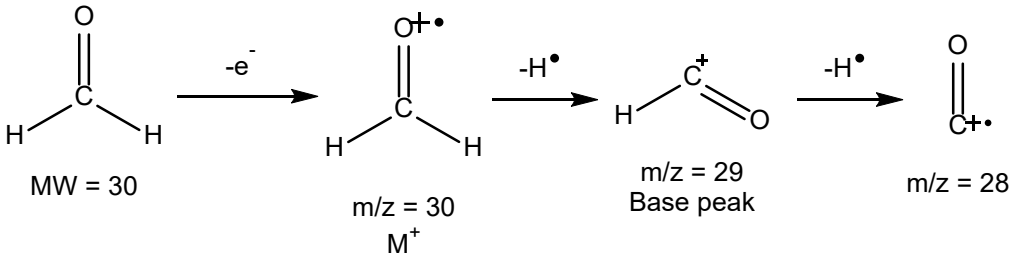

Fig 3. Formaldehyde fragmentation

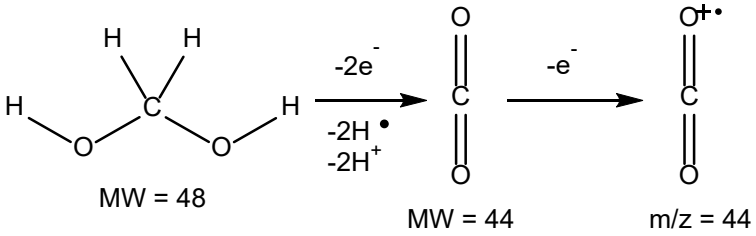

Fig 4. Hydrate of formaldehyde fragmentation

The retention time of peak 2 is 1.943 min with peak area 40.66%. The compound was analyzed using mass spectrometer and gives mass spectrum in Fig. 5. The spectrum shows that peak 2 has 3 major fragments. Fragments with m/z = 32 (molecular ion), m/z = 31 (base line) and m/z = 28 belong to the fragment in methanol fragmentation shown in Fig. 6. The peak 1 could be interpreted as methanol and it is in agreement with MS prediction.

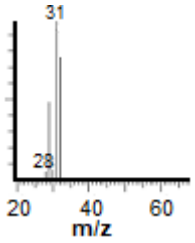

Fig 5. The MS spectrum of peak 2

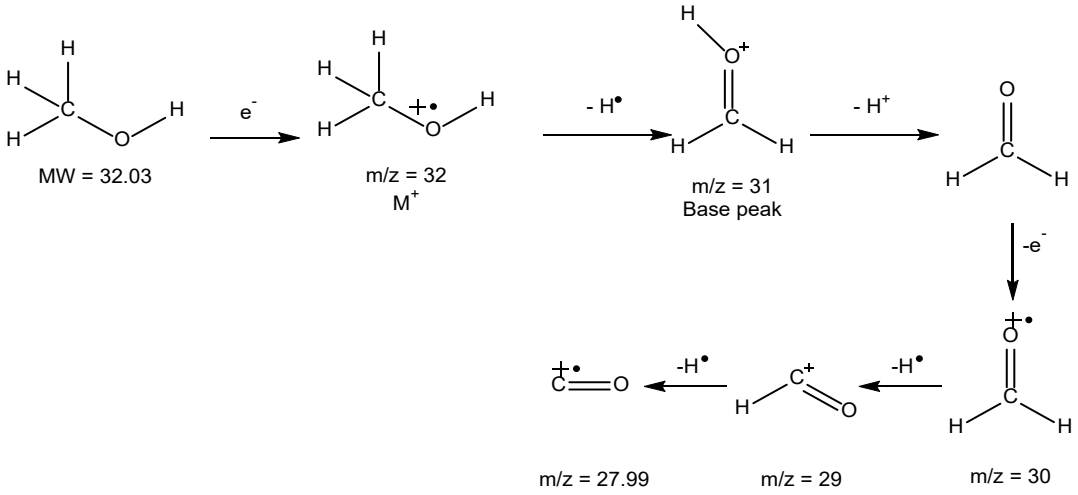

Fig 6. Methanol fragmentation

The time of retention of peak 3 is 1.992 min with peak area 3.59%. The compound was analyzed using mass spectrometer and gives mass spectrum in Fig. 7. That spectrum shows that peak 3 has 4 major fragments. The fragments with m/z = 60 (molecular ion), m/z = 31 (base line), m/z = 44 and m/z = 28 belong to the fragment in methyl methanoate fragmentation presented in Fig. 8. Meanwhile, the reduction of CO_2 could not give an ester as product. The presence of ester in the sample could be occurred because formic acid (expected product from CO_2 photoreduction) and methanol reacted and gives an ester as a product. The existence of methyl methanoate could be interpreted as the existence of formic acid and methanol in the sample. The methanol itself exist as peak 2 in chromatogram and emphasize the presence of formic acid as product of CO_2 photoreduction. Even though the spectrum more accurately interpreted as methyl methanoate, in this paper that peak will be interpreted as formic acid and it is also in agreement with MS prediction.

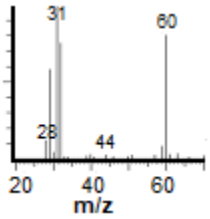

Fig 7. The MS spectrum of peak 3

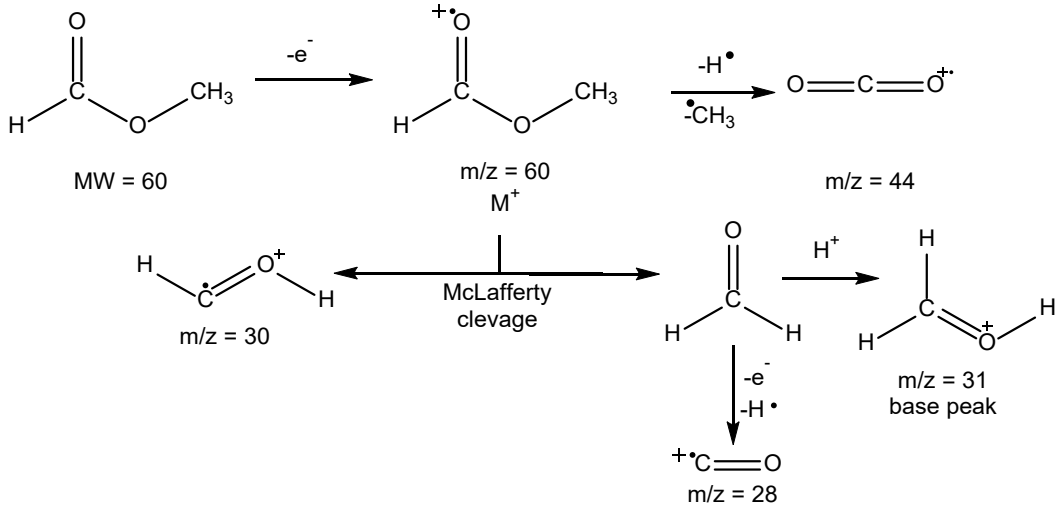

Fig 8. Methyl methanoate fragmentation

The time of retention of peak 4 is 2.108 min with peak area 26.09%. The compound was analyzed using mass spectrometer and gives mas spectrum in Fig. 9. That spectrum shows that peak 4 has a major fragment with m/z = 44. That fragment belongs to that fragment in CO_2 fragmentation displayed in Fig. 10. The peak 4 could be interpreted as unreacted CO_2.

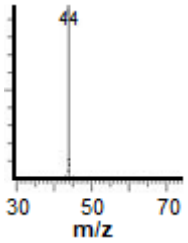

Fig 9. The MS spectrum of peak 4

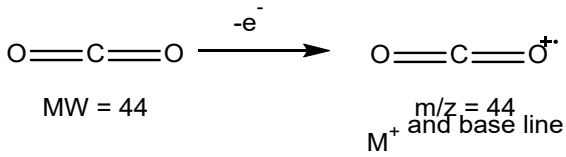

Fig 10. Carbon dioxide fragmentation