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Short communication

# Unravelling the role of Ag—Cr interfacial synergistic effect in Ag/Cr<sub>2</sub>O<sub>3</sub> nanostructured catalyst for the ammoxidation of toluene via low temperature activation of $C_{sp}^3$ -H bond



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ARTICLE INFO	A B S T R A C T				
Keywords: Ag (I) oxide Cr2O3 Nanoparticles Toluene Benzonitrile Ammoxidation Cyanation	An environmentally benign and cost-effective synthesis of benzonitrile is reported by direct oxidative cyanation of aromatic Csp <sup>3</sup> -H bonds of toluene over Ag(I)/Cr <sub>2</sub> O <sub>3</sub> nanostructured catalyst. The catalyst was prepared by a hydrothermal route using cationic surfactant cetyltrimethylammonium bromide and was characterized by powder XRD, XPS, SEM, TEM, TGA, TPD, TPR, UV-visible, FTIR, XANES, and ICP-AES methods. Conjugal effect of Lewis plus Brønsted acidity coupled with Ag—Cr interfacial synergistic interaction appears as detrimental for its high catalytic activity and selectivity (98.4%) for benzonitrile. In situ DRIFTS analysis suggested that the catalytic system proceeded via a reaction pathway explained by Mars-van Krevelen mechanism.				

# 1. Introduction

Direct functionalization of  $C_{sp}^3$ -H hybridized inactive hydrocarbons to form oxygenated products under mild conditions is a major challenge from an industrial point of view [1–8]. Ammoxidation of methylaromatics, an avenue to produce organic nitriles, these have been commercially used as common building blocks that are integral parts for producing pharmaceuticals, agrochemicals and fine chemicals [9–11]. Generally, organic nitriles are synthesized by cyanation of aldehydes using HCN or metalcyanides, which are hypertoxic and cause environmental disasters [11]. Industrially, gas-phase ammoxidation of C—H bond is performed over V—Cr oxides, however, the use of high reaction temperature (>350 °C) and toxic metals refrained from the claims of environmental benignity [12].

The vapor phase ammoxidation of toluene to benzonitrile has been extensively studied as a model reaction and typically with metal and metal oxide catalysts of V, Mo and others [12–21]. Very recently, Iwasawa et al. [22] reported the synthesis of single Cs<sup>+</sup>/Y catalyst which furnished benzonitrile from toluene with very high yield. But so far researchers always wade through several problems embroiled with activity and stability of the catalyst, which further become constraints to its industrialization. Moreover, there is always a competition between ammoxidation and NH<sub>3</sub> oxidation on the catalyst surface, where the latter reaction causes a partial reduction of the oxide surface, particularly at high temperatures [20]. Therefore, control of the rate of unselective oxidation of NH<sub>3</sub> to N<sub>2</sub>/NO<sub>x</sub> is a crucial factor in determining the selectivity of the nitrile product in the ammoxidation reaction [20], because this side reaction limits the availability of surface adsorbed NH<sub>3</sub> (N-insertion) species that are necessary for nitrile formation. It is known that the rate of oxidation of NH<sub>3</sub> is faster than that of the ammoxidation reaction; excess NH<sub>3</sub> modifies the surface oxidation characteristics of a catalyst and decreases the ammoxidation activity [20].

Nevertheless, it is also very difficult to completely avoid  $NH_3$  oxidation but it can only be minimized to the maximum possible extent. Besides, coordinatively unsaturated sites act as Lewis acidic sites for the chemisorption of methyl aromatics and  $NH_3$ . Also, the acidity of the catalyst plays a crucial role in the ammoxidation reaction [17,20]. It is obvious that enhanced acidity is favourable for the better performance of catalysts, as it is known that  $NH_3$  can adsorb on the catalyst surface in the form of either  $NH_4^+$  on Bronsted acid sites or coordinatively adsorbed  $NH_3$  on Lewis acid sites. Furthermore, the strong acidity of the catalyst always leads to the formation of undesired products, such as demethylated products and  $CO_x$  due to the strong adsorption of methyl aromatic compounds [20]. Therefore, it is indispensable to maintain a good balance between the redox and acidic properties of the solid surface to attain high ammoxidation activity and selectivity.

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Since the last decade, Bal and his group has explored the development of Ag-WO3 nanoarchitectures with several morphologies and investigated their activities in C-H activation-based reactions [5,6,23-29]. However, after thorough screening with WO<sub>3</sub> and other members of group VI metal oxides as supports in ammoxidation of toluene, Cr<sub>2</sub>O<sub>3</sub> was chosen to be the best one owing to its activity and long-term stability in the reaction stream. Thus, we came out of this issue for the sustainable production of benzonitrile by means of ammoxidation of toluene using Ag/Cr2O3 nanostructured catalyst, which showed high efficiency of NH3 utilization in the ammoxidation of toluene with very high selectivity (98.4%), a benzonitrile yield of 72%, and sustained activity for 18 h. To the best of our knowledge, this is the highest activity ever shown by a catalyst in terms of activity and stability in the direct benzonitrile production from toluene with O<sub>2</sub> in a singlestep gas-phase reaction at comparatively lower reaction temperature (ca. 280 °C).

# 2. Experimental

# 2.1. Materials and reagents

 $Cr(NO_3)_3.9H_2O$ , AgNO<sub>3</sub>, cetyltrimethylammonium bromide (CTAB), polyvinylpyrrolidone (PVP 10), HPLC grade (~ 9.9%) were purchased from Sigma-Aldrich Co. NH<sub>3</sub>, O<sub>2</sub> and helium gas cylinders were also commercially provided. All the chemicals were used without further purification. Methane was used as an internal standard because it never reacts with the examined catalysts in the present system. Double distilled water was used during the preparation of the catalyst.

# 2.2. Synthesis of catalyst

 $Ag(I)/Cr_2O_3^{CB}$  nanostructured catalyst was prepared according to the protocol described elsewhere [23]. In a typical synthesis procedure, an aqueous solution of 7.9 g of Cr(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O (from Sigma-Aldrich) was dissolved in 27 g of deionized water to give a clear dark blue homogeneous solution. The pH of the solution was kept at 8-9 by gradual addition of a few drops of ammonia solution, and dark green precipitation was finally observed. An ethanolic solution (10%) of 2.7 g of CTAB (from Sigma-Aldrich) was made and allowed to stir at 50  $^\circ C$  for 15 min. The two solutions were mixed maintaining the molar ratio Cr: CTAB:  $H_2O = 1$ : 1: 200. Eventually, a hot solution of 0.094 g AgNO<sub>3</sub> (4% Ag wrt Cr<sub>2</sub>O<sub>3</sub> by weight) and 0.001 g polyvinylpyrrolidone (PVP 10) was added dropwise to the former solution with a dropper. The mixture was allowed to stir for additional 15 min and was subjected to hydrothermal treatment at 180 °C for 24 h in a Teflon-lined autoclave vessel under autogenous pressure. The autoclave was then cooled until it reached room temperature. Then, the green fluffy mixture was taken out as such. The whole mixture was then washed several times with ethanol and dried at 110 °C for 10 h, followed by calcination in air at 750 °C for 6 h (ramped at 1 °C/min) to get eventually green powder of Ag-Cr oxide composite.

# 2.3. Reaction setup

Vapor phase ammoxidation of toluene was carried out at atmospheric pressure using a fixed-bed flow reactor system (Pyrex glass tube) with an inner diameter of 6 mm and externally heated by electric resistances. The reaction temperature was measured inside the catalyst bed by a thermocouple, whose tip was inside the upper side of the catalyst bed. Catalyst powder were pressed to pellets, crushed, and sieved (typically, 0.2 g, sieved into ~500 µm particles) and were packed between quartz wools. Toluene was fed continuously into the gas stream by using a syringe pump. The reactor was fed with a gas mixture of toluene/NH<sub>3</sub>/O<sub>2</sub>/He in the molar (or volume) ratio of 0.2/2.8/1.0/8 with a total volume flow rate (F) of 12.0 mL/min. The conversion and selectivity in the current system were calculated by using methane as an internal standard after considering the fact that methane does not react over the present catalyst up to 500 °C. The individual gas flows were adjusted by mass flow controllers (Brooks). The reaction stream was analyzed by an *online* GC (Agilent), which was equipped with a flame ionization detector (FID), and connected to an HP5 capillary column (30 m length, 0.28 mm i.d., 0.25  $\mu$ m film thickness) for toluene, methane (CH<sub>4</sub>) and benzonitrile analysis, and a thermal conductivity detector (TCD, column Porapak Q column) for O<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, NH<sub>3</sub>, CH<sub>4</sub> and H<sub>2</sub>O analysis.

# 3. Results and discussion

#### 3.1. Catalyst characterization

The Ag-Cr-based catalyst was characterized thoroughly by powder XRD, XPS, SEM, TEM, FTIR, TG-DTG, XANES and ICP-AES. The crystal structure and phase purity of the catalyst were analyzed based on the Xray diffractogram recorded (Fig. 1). The latter showed diffraction peaks at 20 values of 24.44, 33.6, 36.2, 39.8, 41.5, 44.2, 50.2, 54.85, 58.4, 63.5, 65.1, 73.2, 76.9 and 79.1° that can be indexed to the rhombohedral phase of crystalline Cr<sub>2</sub>O<sub>3</sub> (JCPDS 82–1484), thus indicating the presence of trivalent Cr in the sample. From the FWHM of the line broadening corresponding to the diffraction angles and applying Lorentzian peak-fit, we determined (obeying the Scherrer's equation) that the mean crystallite size of the fresh and spent catalyst was 32.3 and 36.1 nm, respectively (Table 1). Similarly, the mean crystallite size of the catalyst prepared under impregnation process (Ag(I)/Cr<sub>2</sub>O<sub>3</sub>  $^{IMP}$ ) was determined to be 52.2 nm, indicating somewhat larger particle size than the former catalyst. Moreover, an intense diffraction peak at  $2\theta$  value of  $32.2^{\circ}$ , followed by some small peaks at  $2\theta$  values of 26.5, 37.9, 54.3 and  $64.6^{\circ}$  corresponding to Ag<sub>2</sub>O crystal faces of (111,110,200), (220,311), respectively, which coincide well with literature values (JCPDS No. 76-1393); thus, denoted as Ag(I)/Cr<sub>2</sub>O<sub>3</sub><sup>CB</sup>. Powder XRD of the spent catalyst also showed that there was no structural deformation or change of oxidation state of the duo species after catalysis, demonstrating the high structural stability of the catalyst.

The presence of other mixed-valent Cr or Ag species in the catalyst was ruled out completely, when the sample was examined in XPS. The wide-scan XPS spectrum (survey spectrum, Fig. 2) of the catalyst depicts



**Fig. 1.** Powder XRD diffractograms of (a) fresh and (b) spent  $Ag(I)/Cr_2O_3^{CB}$  nanostructured catalysts and that of commercial (c) Ag(I) oxide, (d) metallic Ag (0), (e) metallic Cr(0), (f) Cr(VI) oxide and (g) Cr(III) oxide.

#### Table 1

A comparative physicochemical study of Ag(I)/Cr<sub>2</sub>O<sub>3</sub> catalysts.

Catalyst	Oxidation state of	Particle size (nm)		Total acidity		O <sub>2</sub> Uptake
Ag <sup>iaj</sup>	Ag <sup>[a]</sup>	Crystallite size from XRD <sup>[b]</sup> (nm)	Average particle size from TEM <sup>[c]</sup> (nm)	NH <sub>3</sub> Uptake (mmolg <sup>-1</sup> ) <sup>[d]</sup>	Pyridine Uptake (mmolg <sup>-1</sup> ) <sup>[e]</sup>	$(\mu molg^{-1})^{[1]}$
Ag(I)/Cr <sub>2</sub> O <sub>3</sub> <sup>CB</sup>	+ 1	32.3	$26.6\pm0.89$	3.87	0.016	1.09
$\mathop{Ag(I)/Cr_2O_3^{CB}}_{[g]}$	+ 1	36.1	$30.0 \pm 0.9$	-	-	_
Ag(I)/ Cr <sub>2</sub> O <sup>IMP[h]</sup>	+ 1	52.2	500-800	0.15	0.003	0.92

Determined using [a] XPS and Ag *LIII*-edge XANES spectra; [b] Scherrer's equation; [c] TEM histogram; [d]  $NH_3$ -TPD; [e]  $O_2$ -TPD; [f] fresh and [g] spent Ag(I)/Cr<sub>2</sub> $O_3$  catalyst prepared by hydrothermally mediated by cationic surfactant CTAB method, and [h] Ag(I)/Cr<sub>2</sub> $O_3$  catalyst prepared by impregnation method.



Fig. 2. (a) Wide-scan XPS spectrum (survey spectrum), and narrow scan XPS spectrum (core level spectra) of (b) Ag3d, (c) Cr2p and that of (d) O1s in the Ag(I)/  $Cr_2O_3^{CB}$  nanostructured catalyst.

the presence of Ag, Cr and O. From the narrow-high resolution scan XPS spectrum of silver (Ag3d, Fig. 2b) the two symmetric peaks located at 368.4 and 374.4 eV are assigned to the binding energies of Ag  $3d_{5/2}$  and Ag  $3d_{3/2}$ , respectively, indicating only the presence of Ag<sup>+</sup> in the prepared composite [27], which supports the results of powder XRD. The peak at 576.8 and 586.4 eV correspond to Cr  $2p_{3/2}$  and Cr  $2p_{1/2}$ , respectively of the characteristic Cr (III) in the sample (Fig. 2c) [30]. Notably, no XPS peak around 575.8 eV was observed, which certainly thrives out the possibility of the presence of Cr<sup>4+</sup> species on the surface of the catalyst [30]. The O1s signal of the catalyst (Fig. 2d) shows two almost overlapping peaks at 532.2 and 530.2 eV, assigned to lattice oxygen ions in different chemical environments (e.g., Ag<sub>2</sub>O and Cr<sub>2</sub>O<sub>3</sub> respectively). Furthermore, the presence of monovalent Ag<sup>+</sup> species in the catalyst did not change before and after catalysis, as confirmed from

the corresponding Ag *LIII*-edge XANES spectrum (Fig. S1, Electronic Supporting Information, ESI). The nature of edge energies for the fresh and spent catalysts resembled that of  $Ag^+$  valence in  $AgNO_3$  (and not to that with metallic silver foil), that further supports XPS results.

The Ag(I)/Cr<sub>2</sub>O<sub>3</sub><sup>CB</sup> catalyst possesses a regular texture with small and almost homogeneously distributed uniform particles (25–55 nm in size) as imaged by SEM (Fig. S2a, ESI) and TEM (Fig. 2a-c and Fig. S3a, ESI) that was entirely different from that prepared by the impregnation process, which is composed of larger and non-uniform particles (as evident from its TEM image, Fig. S6, ESI). Fig. S3b (ESI) shows broad size distribution (Gauss) of silver particles possessing diameters in the range of 2–5 nm. The mean particles sizes were determined (by Image-J software and Gaussian function) to be 26.6  $\pm$  0.89 nm and 30  $\pm$  0.9 nm, for the fresh and spent Ag(I)/Cr<sub>2</sub>O<sub>3</sub><sup>CB</sup> catalysts, respectively (Table 1 and

Fig. S4a-d, ESI). Thus, the structure-directing effect of CTAB is clearly evident from the SEM analysis. From the EDAX image (Fig. S2b, ESI) it can be seen that the sample contains only Ag, Cr, and O and from the STEM image (Fig. 3d) and the corresponding elemental mapping (Fig. 3e-g) the homogeneous distribution of Ag, Cr and O in the catalyst is demonstrated. The HRTEM image (Fig. 3c) clearly displays the interplanar spacing 0.33 nm, which can be indexed to the (012) plane of Cr<sub>2</sub>O<sub>3</sub> (JCPDS 82-1484) and was easily discriminated from 0.27 nm indexed to (111) plane of Ag<sub>2</sub>O (JCPDS 76-1393). Moreover, the XRD peaks assignment was further confirmed by TEM. The generation of uniformly Ag(I)/Cr2O3 nanoparticles and the thorough dispersion of supported silver nanoparticles are attributable to the use of the cationic surfactant of CTAB. Therefore, the important role of CTAB in controlling the formation of nano architectures of  $Ag(I)/Cr_2O_3^{CB}$ , under the so called "Template Effect", cannot be avoided. The embedding of CTAB molecules on the pre-calcined catalyst surface was further confirmed from TGA analysis (Fig. S7, ESI) and ex-situ Fourier Transform Infrared (FTIR) analysis (Fig. S8, ESI).

#### 3.2. Catalytic performance

Spurred by the earlier reports, we started screening the activities of several Cr-based catalysts from 200 °C (Table 2) in the ammoxidation of toluene with  $(O_2+ NH_3)$  reaction in the fixed bed reactor. From 200 to 250 °C, no catalyst showed any activity. Even neat reaction (Table 2, Entry 1) was performed to check the necessity of the catalyst, but neither benzonitrile (PhCN) nor any oxygenate (e.g. benzaldehyde/ benzoic acid) was detected. Commercial catalysts, like Cr(III) oxide, Cr(VI) oxide, metallic chromium, Ag(I) oxide, metallic silver (Table 2, Entry

2–6) totally failed to show any catalytic activity, even at 280 °C. However, the catalyst prepared under the impregnation process (Ag(I)/ $Cr_2O_3^{IMP}$ ) taking commercial  $Cr_2O_3$  as support, showed very poor activity (Table 2, Entry 7); although, similarly prepared catalyst (Ag(0)/ $Cr_2O_3^{IMP}$ ) with metallic Ag(0) as active site failed to do so (Table 2, Entry 8), demonstrating the importance of cationic silver in the reaction.

Then the prepared  $Ag(I)/Cr_2O_3^{CB}$  catalyst was tested under the same reaction conditions. Although this catalyst exhibited same elemental composition and corresponding metal oxidation states, and similar loading of silver, it was proved much superior to the Ag(I)/Cr\_2O\_3^{IMP} catalyst, furnishing 73.1% conversion of toluene with PhCN selectivity of 98.4% (yield = 72%, Table 2, Entry 10). Interestingly, the catalyst provided stable activity for 18 h without any significant activity loss. After 18 h, the catalytic activity started decreasing. This experimental finding can be attributed to two major facts. After 18 h, continuous decrease of PhCN selectivity was observed due to the increased formation of benzamide, apart from CO<sub>2</sub>; this fact demonstrates the formation of excess water that facilitated nucleophilic substitution mechanism [12]. Perhaps, the formed benzamide blocked the access of reactants to active metal i.e. Ag(I) surface sites, and interrupted the involved redox catalysis. Moreover, accumulation of coke was also formed that probably encapsulated Ag(I) surface sites and thereby completely deactivated the catalytic system. TGA analysis (Fig. S7c, ESI) of the spent catalyst (after 18 h) revealed a mass loss ~8% and the major loss was noticed in the 180°-450 °C range, indicating a considerable amount of coke deposition that accounted for catalyst deactivation. The catalyst showed 67.0% toluene conversion with PhCN selectivity of 90.2% (Table 2, Entry 11).

It was also noticed that when the loading of Ag was increased to



Fig. 3. TEM images (a-c) in ascending resolution, and (d) STEM image and STEM-EDS elemental mapping of (e) Ag, (f) Cr and that of (g) O in the Ag(I)/ $Cr_2O_3^{CB}$  nanostructured catalyst.

#### Table 2

Catalytic performances in selective ammoxidation of toluene to benzonitrile reaction over various Ag-Cr-based catalysts.<sup>a</sup>

Entry	Catalyst	С <sub>т</sub> (%) <sup>b</sup>	S <sub>BN</sub> (%) <sup>c</sup>	Y <sub>BN</sub> (%) <sup>d</sup>	TOF (h <sup>-1</sup> ) <sup>e</sup>	NH <sub>3</sub> Reacted/ PhCN Formed
1	No					
	Catalyst					
2	$Cr_2O_3^{COM}$	-	-	-	-	-
3	$CrO_3^{COM}$	-	-	-	-	-
4	Cr(0) <sup>COM</sup>	-	-	-	-	-
5	Ag <sub>2</sub> O <sup>COM</sup>	-	-	-	-	-
6	Ag(0) COM	-	-	-	-	-
7	Ag(I)/	4.1	16.4	0.67	1.8	253
	$Cr_2O_3^{IMP}$					
8	Ag(0)/	-	-	-	-	-
	$Cr_2O_3^{IMP}$					
9 <sup>r</sup>	Ag(I)/	63.2	88.9	56.2	27.5	2.9
	$Cr_2O_3^{CB}$					
10	Ag(I)/	73.1	98.4	71.9	31.9	3.2
~	$Cr_2O_3^{CB}$					
11 <sup>8</sup>	Ag(I)/	67.0	90.2	60.4	29.2	5.2
ь	$Cr_2O_3^{CB}$					
12 <sup>11</sup>	Ag(I)/	45.7	83.8	38.3	19.9	4.5
	$Cr_2O_3^{CB}$					
13	Ag(I)/	-	-	-	-	-
1	$Cr_2O_3^{CB}$					
14	Ag(I)/	88.0	95.5	84.0	38.4	0.8
	$Cr_2O_3^{CB}$					

<sup>a</sup> Reaction Conditions: toluene/O<sub>2</sub>/NH<sub>3</sub>/He = 0.2: 1.0: 2.8: 8.0 mL/min; catalyst weight = 0.2 g; loading of Ag = 3.8 wt%; reaction temp = 280 °C.

 $^{b}$  C<sub>T</sub> = conversion of toluene based upon the FID-GC (GC equipped with a flame ionization detector), and is equal to 100  $\times$  (mol of toluene reacted)/ (initial mol of toluene used).

 $^{c}~S_{BN}$  = is the selectivity of PhCN and is equal to 100  $\times$  (total mol of PhCN)/ (total mol of toluene consumed).

 $^d~Y_{BN}$  is the yield of PhCN and is equal to (C  $_T \times$  S  $_{BN})/$  100.

<sup>e</sup> TOF is defined as reacted toluene(mol)/total metal (mol)/h.

 $^{\rm f}$  toluene/O\_2/NH\_3/He = 0.4: 1.0: 2.8: 8.0 mL/min.

<sup>g</sup> After 18 h.

 $^{\rm h}\,$  Loading of Ag = 9.8 wt%.

<sup>i</sup> p-Nitrotoluene.

<sup>j</sup> Benzaldehyde was used as feedstock, respectively.

~10%, the catalyst was able to furnish PhCN with 38.3% yield (Table 2, Entry 12). The drastic increment of Ag(I) oxide particle size (confirmed from TEM images, Fig. S5, ESI) with higher loading, probably accounts for this experimental finding. Moreover, when benzaldehyde was used as feedstock under ammoxidation conditions, it led to the formation of PhCN with high yields and much higher rates than toluene itself (Table 2, Entry 13).

To get insight of the superiority of  $Ag(I)/Cr_2O_3^{CB}$  catalyst over Ag(I)/ $Cr_2O_3^{IMP}$ , we integrated several characterization results (Fig. S3-S12, ESI) of these two catalysts. Thorough dispersion of Ag nanoparticles in Ag(I)/  $Cr_2O_3^{CB}$  catalyst, may be one of the key reasons of its superiority, because smaller crystallites in Ag(I)/Cr<sub>2</sub>O<sub>3</sub><sup>CB</sup> catalyst offered a higher density of coordinatively unsaturated sites. We also investigated their comparative acidic character by means of NH3-TPD (Fig. S12a, ESI) from 80 °C-650 °C. The TPD peaks for NH<sub>3</sub> on Ag(I)/ $Cr_2O_3^{IMP}$  were observed between 205  $^{\circ}\text{C}$  -450  $^{\circ}\text{C}$  with three maxima at 205, 327 and 450  $^{\circ}\text{C}\text{;}.$  On the other hand, for the Ag(I)/Cr $_2O_3^{CB}$  catalyst, NH $_3$ -TPD curve was observed within a broad range, ca. 250 °C-530 °C, with maxima at 487 and 527 °C, demonstrating the fact that the overall (Lewis + Brønsted) surface acidity of  $Ag(I)/Cr_2O_3^{CB}$  catalyst was greater than that of  $Ag(I)/Cr_2O_3^{CB}$ Cr<sub>2</sub>O<sub>3</sub><sup>IMP</sup> catalyst. From their respective calibration curves, it was calculated that the amount of desorbed NH3 over these catalysts was 3.868 and 0.155 mmol  $g_{cat}^{-1}$  respectively, demonstrating that  $\sim\!\!25$  times greater concentration of acidic sites is present in the former catalyst (Ag  $(I)/Cr_2O_3^{CB}$ ; and this contribution majorly comes from the surface of Cr<sub>2</sub>O<sub>3</sub> [31], which also believed to act as a textural promoter that prevents sintering of the Ag(I) oxide and, hence, the surface area of the catalyst is preserved during catalysis [32].

The Lewis acid sites in the catalyst coordinatively adsorb NH<sub>3</sub> and toluene as well [16] and compel them to get reacted with the active site present (e.g.  $Ag^+$ ). We also conducted toluene TPD over these two catalysts and noticed that the quantitative amount of desorbed toluene for these catalysts were 0.058 mmol g<sup>-1</sup> and 0.021 mmol g<sup>-1</sup>. That means the amount of toluene adsorbed is ~3 times greater on the Ag(I)/Cr<sub>2</sub>O<sub>3</sub><sup>CB</sup> than Ag(I)/Cr<sub>2</sub>O<sub>3</sub><sup>IMP</sup> catalyst. Furthermore, from H<sub>2</sub>-TPR (Fig. S13, ESI), it was detected that the Ag-species were reduced at higher temperatures compared to the commercial Ag<sub>2</sub>O, demonstrating high interaction of Ag<sup>+</sup> and Cr<sub>2</sub>O<sub>3</sub> in the Ag(I)/Cr<sub>2</sub>O<sub>3</sub><sup>CB</sup> catalyst; therefore, one can attribute the catalytic discrepancies in terms of the interface between the support and active metal (here Ag<sup>+</sup> NP), that plays pivotal roles in the ammoxidation reaction.

### 3.3. Reaction mechanism

It is generally agreed that activation of the methyl group is the RDS during toluene ammoxidation [13]. The nature of this activated species, however, is still under debate. Meanwhile, introducing p-nitrotoluene as substrate (Table 2, Entry 13), furnished only CO<sub>2</sub>, which strongly provoked the involvement of heterolytic C-H rupture producing a carbocationic intermediate, and this hypothesis got rendered by spectroscopic evidence (in situ DRIFTS, Fig. S14, ESI). Even after seizing toluene flow, we speculated the formation of benzaldehyde, which certainly indicates the fact that the catalyst (Ag<sup>+</sup> species) is capable of activating the C—H bond of toluene without the intervene of NH<sub>3</sub>. These experimental findings also compel us to hypothesis that the surface lattice oxygen induces toluene oxidation reaction, and gaseous oxygen species accelerate the replenishment and migration of reactive oxygen species through an oxygen vacancy. In contrast,  $Ag(I)/Cr_2O_3^{IMP}$  catalyst needs the direct dissociation of O2 on the surface of the catalyst for toluene oxidation and produces large concentration of CO2 as a consequence. Also, the detection of benzaldehyde (benzyl species) as previously observed by Azimov et al. [33] demonstrates the fact that probably it served as intermediate that reacts with NH<sub>3</sub> to produce PhCN, and C-H activation in toluene is the RDS. This was evidenced by when benzaldehyde itself, which gave a very similar IR spectrum evidence (Fig. S15, ESI). Since the formation rate of PhCN by ammoxidation of benzaldehyde was much higher than that by toluene (Table 2, Entry 14), this suggests that the proposed mechanism, including the partial oxidation of toluene to benzaldehyde, is the RDS. Had benzyl species been intermediate, a degree of surface reduction of the catalyst is expected [33], again, which is contradicting the H2-TPR results (Fig. S13, ESI)., because Ag<sup>+</sup> species present in the catalyst is not easily reducible compared to the commercial Ag<sub>2</sub>O; therefore, partial reduction of Ag<sup>+</sup> species is highly expected as observed in Mars-van Krevelen mechanism [12-21].

Therefore, we can assume that acidic sites in the  $Ag(I)/Cr_2O_3^{CB}$ catalyst coordinatively adsorb  $\pi$ -cloud density of toluene and to some extent few NH<sub>3</sub> molecules (chemisorbed) [14] to generate NH<sub>4</sub><sup>+</sup> ions that are able to intervene in the ammoxidation mechanism, by increasing the nucleophilic character of oxygen surface sites, and interacting with the -Me groups, making them prone towards activation [34]. Adsorbed toluene produces a carbocationic intermediate and an H<sup>-</sup> ion on the Ag (I)- active site via heterolytic C-H bond rupture, and the latter reduces it (Ag(I)- active site in silver cluster) [35] partially; however, although Cr<sub>2</sub>O<sub>3</sub> does not take part in this redox-system directly, its dehydrogenative-character assists the C-H heterolytic cleavage and stabilizes the H<sup>-</sup> ion. The lattice oxygen takes part in the oxidation process, resulting in the formation of an alkoxide type intermediate, which then undergoes H<sup>-</sup> abstraction by silver cluster to give a benzyltype intermediate that easily gets cyanation by NH<sub>4</sub><sup>+</sup> ions and thus the entire mechanistic process might proceed through the Mars-van Krevelen mechanism. Importantly,  $Ag^+$  (present in  $Ag(I)/Cr_2O_3^{CB}$ ) or strong Ag-Cr interfacial synergistic interaction (suspected to have generated from H<sub>2</sub>-TPR  $\sim$  200–280 °C) that refrain from its (NH<sub>3</sub>) oxidation, because if NH<sub>3</sub> could easily reduce Ag(I) center, massive production of N<sub>2</sub> (or NO<sub>x</sub>) would have been detected. The existence of a strong synergistic effect at the interface sites between  $Cr_2O_3$  and Ag(I)-nanoparticles probably plays the key factor for making it highly active, selective, and a robust Ag(I)/ $Cr_2O_3^{CB}$  hetero-nanostructured catalytic system. However, more studies concerned with the role of surface lattice oxygen are highly required in the future to reveal the reaction mechanism by integrating several in situ techniques and DFT, followed by further optimization of the catalytic performance of the Ag(I)/ $Cr_2O_3$  catalyst for real industrial applications.

# 4. Conclusions

Ag(I)/Cr<sub>2</sub>O<sub>3</sub> catalysts have been successfully prepared in a hydrothermal route in a surfactant mediated process. The significant features of the catalyst lie in its high efficiency of NH<sub>3</sub> utilization in the ammoxidation of toluene reaction and its activity in furnishing benzonitrile with a high yield (72%) at comparatively lower reaction temperature (280 °C) with O2 in single-step gas-phase reaction. The existence of a strong synergistic effect at the interface sites between Cr<sub>2</sub>O<sub>3</sub> and Ag(I)-nanoparticles probably plays the key factor in the inhibition of NH<sub>3</sub> oxidation, thereby making it highly active, selective and a robust hetero-nanostructured catalytic system. Understanding the effect of different functional groups in the aromatic system and mode of synergism in the catalyst alongside the acidity effects using DFT, is the aim of further studies and the results of which will be reported in a future publication. The work delineates a sustainable strategy for synthesizing benzonitrile while avoiding conventional toxic cyanides at mild conditions.

# **CRediT** author statement

Shankha Shubhra Acharyya: Conceptualization, Conducted Experiments and Draft-writing.

**Shilpi Ghosh:** Conducted Experiments, Catalyst Characterization & Interpretation and Draft-writing.

**Ms. Rubina Khatun** did few catalytic experiments and analyzed the products using gas chromatograph and also helped in chatacterization of the catalyst (XRD, TEM analysis).

Rajaram Bal (Corresponding Author): Reviewing and Editing.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

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## Appendix A. Supplementary data

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