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Study on the conversion of glycerol to nitriles over a $Fe_{19.2}K_{0.2}/\gamma\text{-Al}_2O_3$ catalyst

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ABSTRACT

An Fe_{19.2}K_{0.2}/ γ -Al₂O₃ catalyst for the catalytic amination of glycerol to propionitrile was prepared. Acetonitrile as a major product was obtained over this catalyst from the amination of glycerol. Additionally, propionitrile, ethylene and propylene were also obtained. The parameters influencing the catalyst performance were studied thoroughly, and an optimised process for the amination of glycerol to acetonitrile and propionitrile over the catalyst was obtained. Under the optimised conditions, which were a reaction temperature of 525 °C, an atmospheric pressure with an ammonia/glycerol molar ratio of 8:1 and GHSV of 1338 h⁻¹, the total yield of acetonitrile and propionitrile was 58.4%, and the converted amount of glycerol over one gram of catalyst reached 0.42 g h⁻¹. The catalyst was characterised by XRD, XPS, TEM and IR of the adsorbed pyridine. The characterisation results indicated that the dehydration reaction in the tandem reaction mainly occurred on the Lewis acid sites and revealed that both Fe₂O₃ and Fe₃O₄ are active species for the dehydrogenation of imines to nitriles, but the former is more active than the latter. It also revealed that the catalyst deactivation was due to carbon deposits, the transformation of Fe₂O₃ to the Fe₃O₄ phase, as well as agglomeration of the Fe₂O₃ or Fe₃O₄ phase during the catalytic run and regeneration process.

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1. Introduction

Due to the continuing decline in fossil fuel resources and increasing concerns over greenhouse gas emissions and energy security, there has been a resurgence of interest in renewable bio-energy. Currently, because of its environmental benefits and little impact on engine performance, biodiesel has become one of the best alternatives to reduce the world's dependence on fossil fuel. Biodiesel is produced by the transesterification of vegetable oils, where approximately 100 kg glycerol is obtained as the major by-product for every 900 kg of biodiesel produced [1,2]. With the rapidly growing use of biodiesel, glycerol has become available in excess. Attempts at converting low-cost glycerol to commercially valued products, including 1,2-propanediol, 1,3-propanediol, acrolein, lactic acid, aromatics, acrylonitrile, and ethylene glycol, have been made [3]. Among all of the transformations, the conversion of glycerol to acrolein is the most studied [4]. The double dehydration of glycerol to acrolein can be achieved using a great variety of acid catalysts [5–22]. In 2008, Guerrero-Pérez et al. [23] found that glycerol can be converted to acrylonitrile with a selectivity of 58.3%

and a glycerol conversion of 82.6% by an ammoxidation process over a VSbNb/Al catalyst. Three elementary reactions are involved in the transformation (Scheme 1). First, glycerol is doubly dehydrated to acrolein. Then, acrolein condenses with ammonia to generate the intermediate imine. Finally, the imine is converted to acrylonitrile by oxidative dehydrogenation.

Additionally, the synthesis of allyl alcohol from glycerol has been reported very recently [24–26] and revealed that the conversion of glycerol to allyl alcohol is through dehydration and consecutive hydrogen transfer catalysed by transition metal oxides, such as iron oxide and methyltrioxorhenium.

Nitriles, such as acetonitrile, can be synthesised from alcohols by two approaches: amination–dehydrogenation [27,28] and ammoxidation [29,30]. In recent years, we have successfully synthesised C2 and C4 nitriles through the amination–dehydrogenation of ethanol [28,31] and butanol [32] over a CoNi/ γ -Al₂O₃ catalyst; we have also succeeded in the synthesis of phenylacetonitrile [33] and propionitrile [34] over a ZnCr/ γ -Al₂O₃ catalyst through the amination–dehydrogenation of styrene oxide and allyl alcohol, respectively. The pathways for the transformation of allyl alcohol to propionitrile are shown in Scheme 2 [34]. First, allyl alcohol is dehydrogenated to acrolein. After the formation of acrolein, there are two possible pathways that yield propionitrile. One is the condensation of acrolein with ammonia to give the







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Scheme 1. The pathway for the formation of acrylonitrile from the ammoxidation of glycerol.



Scheme 2. Pathways of allyl alcohol to propionitrile through amination-dehydrogenation.

intermediate imine, which is then dehydrogenated to generate acrylonitrile and hydrogen: the carbon–carbon double bond in the acrylonitrile molecule is hydrogenated with the hydrogen generated from the dehydrogenation of the imine and alcohol to produce propionitrile. The other pathway involves the hydrogenation of acrolein with the generated hydrogen to give propionaldehyde. Then, the propionaldehyde condenses with ammonia and is dehydrogenated to give propionitrile.

Scheme 2 shows that acrolein is a key intermediate in the preparation of propionitrile from allyl alcohol. As referred to above, the conversion of glycerol to acrolein has been achieved using various catalysts [5–22]. It is expected that the transformation of glycerol to propionitrile is possible if we integrate the double dehydration of glycerol to acrolein (or through allyl alcohol) and the amination of acrolein to propionitrile reaction over a multifunctional catalyst. Herein, we report the selection, characterisation, and catalytic testing of the catalysts to pursue the above goal.

2. Experimental section

2.1. Catalyst preparation

The metal nitrates $Fe(NO_3)_3 \cdot 9H_2O$ (98.5%), $Cu(NO_3)_2 \cdot 3H_2O$ (99%), Co(NO₃)₂·6H₂O (99%), Zn(NO₃)₂·6H₂O (99%), Cr(NO₃)₃·9H₂O (99%), Ni(NO₃)₂·6H₂O (98%), KNO₃ (99%), NaNO₃ (99%), Mg(NO₃)₂ ·6H₂O (99%), Ca(NO₃)₂·4H₂O (99%), Sr(NO₃)₂ (99.5%) and other reagents used for preparation of the catalysts were obtained from KRS Chemical Reagent Cooperation, Tianjin, China. The catalyst support γ -Al₂O₃ (99.5%) was provided by the Tianjin Research and Design Institute of Chemical Industry, Tianjin, China. TiO₂ (99%) and ZrO₂ (99%) were obtained from Tianjin Chemical Reagent Factory, Tianjin, China. The catalysts with the γ -Al₂O₃ as support were prepared by kneading a mixture of γ -Al₂O₃ with an aqueous solution of the corresponding transition-metal nitrates, followed by extruding, drying and calcination. For example, the catalyst $Fe_{19.2}K_{0.2}/\gamma$ -Al₂O₃ was prepared as follows: in a beaker placed in a water bath at 100 °C, 28.9 g of $Fe(NO_3)_3 \cdot 9H_2O$ and 0.1 g of KNO₃ were added, and a small amount of distilled water (less than 2 mL) was added to dissolve the nitrates. To the solution was added 16.0 g γ -Al₂O₃. The mixture was kneaded for 3 h in a kneader and the resulting kneaded material was processed in an extruder to obtain extrudates with a diameter of 2 mm and a length of 2.5 mm. The catalyst precursors were dried at 100 °C for 6 h and calcined at 550 °C for 6 h to obtain the catalyst.

2.2. Catalyst characterisation

The X-ray diffraction (XRD) patterns of the samples were recorded with a Rigaku D/max 2500 X-ray diffractometer using Cu K α radiation (40 kV, 150 mA) in the range 2θ = 10–90°. X-ray photoelectron spectroscopy (XPS) was performed with a PHI 1600 spectroscope using Al K α X-ray source for excitation. The carbon C1s peak at 284.6 eV was used as a reference for the charge correction. By fitting a Gaussian–Lorentzian (GL) function, a deconvolution of the Fe $2p_{3/2}$ peak of the catalyst was performed. The GL-function was fitted to the experiments. The Fe²⁺ and Fe³⁺ peaks were fixed at 709.27 and 710.88 eV, respectively. The Gaussian–Lorentzian ratio was fixed at 90, meaning 90% Gaussian and 10% Lorentzian. The full width at half maximum (FWHM) was set to 2.2 eV.

Transmission electron micrographs (TEM) were obtained on a JEOL 100CX-II instrument equipped with an energy dispersive X-ray (EDX) detector (Oxford Instruments) at an accelerating voltage of 200 kV. Specimens for TEM analysis were prepared by ultrasonic dispersion in ethanol where a drop of the resultant suspension was evaporated on a lacey-carbon/Cu grid. The surface area, total pore volume and pore size distribution of the catalysts were measured at 77 K by nitrogen adsorption using a Micromeritics ASAP 2020 Surface Area and Porosity Analyser.

The IR spectra of adsorbed pyridine were recorded using a Thermo Nicliet Nicolet Nexus 470 spectrometer equipped with a heatable and evacuatable IR cell with CaF₂ windows, connected to a gas dosing–evacuating system. The powdered samples were pressed into self-supporting wafers with a diameter of 20 mm and a weight of 50 mg. Prior to analysis, all samples were pretreated at 400 °C for 1 h, under high vacuum conditions (5×10^{-5} Pa), followed by cooling to 200 °C. Then, pyridine was adsorbed at this temperature for 15 min. The physisorbed pyridine was removed by evacuating during 1 h at 200 °C, under high vacuum conditions (5×10^{-5} Pa). Then the infrared spectra were recorded.

For determining the metal content, the sample was first dissolved in aqua regia (HNO_3 -HCI) and HF, and then the metal content of the solution was analysed by a T.J.A. ICP-9000(N + M) type ICP-AES instrument.

Thermogravimetric-different scanning calorimetry (TG-DSC) measurement was carried out on a Perkin Elmer-7 thermogravimetric analyser from 20 to 790 °C with the rate of 10 °C min⁻¹ under air atmosphere.

2.3. Catalyst test

Catalytic tests were conducted in a continuous fixed-bed reactor. Specifically, 15.0 mL of the catalyst sample was loaded into a reactor (i.d. = 15 mm; length = 1000 mm), which created a catalyst zone of approximately 85 mm in the middle part of the reactor. The temperature in the catalyst zone was kept constant and was measured using a thermocouple located in the centre of the catalyst bed. An aqueous solution of 20 wt% glycerol was prepared from 99.3 wt% glycerol obtained from KRS Chemical Reagent Cooperation, Tianjin, China. In the catalytic run, the aqueous solution of 20 wt% glycerol was pumped into the reactor by a syringe pump, and the flux of ammonia (99%) was regulated by a PID cascade controller (STP 220 mL/min). The liquid products were separated with a gas–liquid separator after collection in a condenser, and the gaseous products generated at certain periods of time were collected after passing through an absorber with water to remove the entrained low boiling point liquid products for analysis. The products were identified by gas chromatography–mass spectrometry (HP5971 GC–MS) with a 30 m SE-30 capillary column.

The products were analysed by a gas chromatograph equipped with a 30-metre DB-5 capillary column. The content of each liquid product was calculated using calibration curves with *n*-butanol as an internal standard. The GC temperature program was 70 °C for 3 min and 40 °C/min up to 100 °C. To analyse accurately, the content of the glycerol was analysed with cyclohexanol as an internal standard. The GC temperature program was as follows: 100 °C for 2 min, 40 °C/min up to 200 °C. The contents of the gaseous products, except carbon dioxide, were determined by the external standard method.

The content of CO_2 in the reaction solution (present in the form of ammonium carbonate) was determined by a titration method (ISO 3422-1975 (E)): 5.00 g (weighed to the nearest 0.001 g) of the reaction solution was treated with a carbonate-free sodium hydroxide solution (400 g/L) and then boiled for 15 min to eliminate ammonia. After cooling to room temperature, 25 mL of a barium chloride solution (100 g/L) and 0.2 mL of a thymolphthalein solution (1 g/L) were added to obtain sedimentation of CO₂. This solution was neutralised with a standard volumetric hydrochloric acid solution (0.5 N) until the solution was decolourised. Then, 0.2 mL of methyl red solution and an excess standard volumetric hydrochloric acid solution (0.5 N) of V_1 mL were added to the solution and boiled for 5 min to eliminate carbonic acid. The cooled solution was back-titrated using the standard volumetric sodium hydroxide solution (0.5 N) until the yellow end-point of the indicator was reached. The volume of the standard volumetric sodium hydroxide solution consumed was V_2 mL. The content of CO_2 in the reaction solution was then calculated using the following equation from V_1 and V_2 .

Moles of CO₂ in reaction solution =
$$\frac{c_1V_1 - c_2V_2}{1000 \times 2 \times 5.00} \times m_{out}$$

where c_1 is the actual concentration of the 0.5 N standard volumetric hydrochloric acid solution; c_2 is the actual concentration of the 0.5 N standard volumetric sodium hydroxide solution; m_{out} is the mass of reaction solution

Glycerol conversion (%) = [(moles of glycerol pumped – moles of unconverted glycerol)/mole glycerol pumped] \times 100

 $\label{eq:product} \begin{array}{l} \mbox{Product selectivity (\%)} = [moles \mbox{ of the product}/(moles \mbox{ of } $$ glycerol pumped - moles of unconverted $$ glycerol)] \times 100 \end{array}$

In the case of carbon dioxide, the selectivity is calculated by the following equation.

 $\begin{array}{l} \mbox{Selectivity of CO}_2 \ (\%) = [moles \ of \ CO_2/3 (moles \ of \ glycerol \ pumped \\ - \ moles \ of \ unconverted \ glycerol)] \times 100 \end{array}$

Carbon balance (%) = [sum of moles of carbon in the identified products/moles of carbon in converted glycerol] \times 100

3. Results and discussion

3.1. Selection of catalyst

The initial goal of this work was to find an integrated catalyst that could catalyse the reaction of glycerol with ammonia to propionitrile. Theoretically, the reaction should proceed as shown in Scheme 3. Therefore, the catalyst should have the functions of the double dehydration of glycerol to acrolein, dehydrogenation of imines and hydrogenation of carbon–carbon double bonds with the hydrogenation generated in situ from the above dehydrogenation.

 γ -Al₂O₃ [35], TiO₂ [8] and ZrO₂ [7] can catalyse the double dehydration of glycerol to acrolein, and some transition metals, such as cobalt, zinc, iron and copper, can dehydrogenate imines to nitriles in the amination of alcohols and can promote the hydrogenation of carbon–carbon double bonds [31,34,36,37]. Therefore, γ-Al₂O₃, TiO₂, and ZrO₂ were chosen as supports, and several transition metals, including chromium, iron, cobalt, nickel, copper, and zinc, were used as dehydrogenation-hydrogenation active components to prepare the multifunctional catalysts for the transformation of glycerol to propionitrile. Initially, several mono-metallic catalysts containing 20% different metals on γ -Al₂O₃ were prepared. Their catalytic performances in the reaction of interest were evaluated, and the results are presented in Table 1 (Table 1, entries 1-6). The glycerol conversions over the catalysts were higher than 94% under atmospheric ammonia pressure at 475 °C. However, the selectivity towards propionitrile was low for all of the catalysts. Among the catalysts, those with iron and chromium as active components (Fe_{19.5}/ γ -Al₂O₃ and Cr_{19.8}/ γ -Al₂O₃) gave better results: the selectivity towards propionitrile was higher than 11% (entries 1, 5) in these cases. The reaction mixture was subjected to GC-MS analysis. The results indicated that acetonitrile, ethylene, and propylene were the organic products in the reaction mixture and that acetonitrile was the main product. Additionally, carbon dioxide was produced. Quantitative analysis of the identified products was performed and the carbon balance was obtained for the catalysts. The results indicated that the catalyst $Fe_{19.5}/\gamma$ -Al₂O₃ was the best. Its total selectivity towards propionitrile and acetonitrile was higher than 51%, and the overall selectivity of the identified organics and carbon balance reached up to 66.9% and 75.0%, respectively. The other catalysts showed low selectivity towards organic products and carbon balance. Due to the good performance of iron compared to other transition metals, catalysts with iron supported on ZrO₂ and TiO₂ were also prepared. The catalytic results revealed that Fe_{19.5}/ γ -Al₂O₃ showed the best performance of the three catalysts (Table 1, entries 1, 7, 8). Therefore, the effect of iron content on the catalysis was studied in more detail to optimise the catalytic performance. A series of catalysts with different iron contents were prepared and tested. The catalytic test results are given in Table 1. Iron is necessary for the transformation of glycerol to propionitrile and acetonitrile (Table 1, entry 9). The selectivity of both propionitrile and acetonitrile increased with the increase in the iron content (Table 1, entries 1, 9-12), reaching maximums of 40.7% and 11.5%, respectively, when the iron content was 20%. The selectivity then decreased as the iron content was further increased. Additionally, the selectivity of carbon dioxide increased with the iron content within the test range.

Further investigation was focused on improving the performance of the catalyst $Fe_{19.5}/\gamma$ - Al_2O_3 by doping with alkali or alkaline earth metals. The test results of the catalysts doped with different metals are presented in Table 2. The doping of the metals had no obvious effect on the selectivity of propionitrile but decreased the selectivity of acetonitrile in most cases. Meanwhile, the selectivity of propylene was improved in many cases. In all cases, the formation of carbon dioxide was suppressed to some degree. The doping of 0.2% potassium not only increased the selectivity of acetonitrile by 1% but also increased the selectivity of acetonitrile by 1% but also increased the selectivity of propylene by more than 3% (Table 2, entry 5). In this case, the total selectivity towards propionitrile and acetonitrile was higher than 53%, and the overall selectivity of the identified organics reached 70.7%. Increasing or decreasing the potassium content did not re-



Scheme 3. The transformation of glycerol to propionitrile in principle.

 Table 1

 Performances of the selected catalysts on the glycerol amination reaction.

Entry	Catalyst	Conversion (%)	Selectivity	Selectivity (%)					Carbon balance (%)
			MeCN	EtCN	C_2H_4	C_3H_6	CO ₂		
1	$Fe_{19.5}/\gamma$ - Al_2O_3	99.0	40.7	11.5	4.9	9.8	23.3	51.7	75.0
2 ^a	$Co_{19.4}/\gamma - Al_2O_3$	99.4	40.5	8.6	4.4	2.2	20.6	48.8	61.2
3	$Ni_{20.1}/\gamma$ - Al_2O_3	97.7	41.0	9.7	3.0	2.0	11.8	49.5	52.0
4 ^a	$Cu_{19.7}/\gamma - Al_2O_3$	98.6	29.1	3.8	2.3	0.4	10.3	32.4	35.4
5 ^a	$Cr_{19.8}/\gamma - Al_2O_3$	94.4	37.9	11.2	4.8	2.4	12.2	33.7	54.2
6 ^a	$Zn_{20,2}/\gamma$ - Al_2O_3	97.0	28.7	6.0	2.0	1.0	15.7	34.1	43.2
7	Fe _{19.6} /ZrO ₂	98.9	26.4	5.3	0.4	1.4	25.6	31.4	50.2
8	Fe _{19.1} /TiO ₂	99.3	27.2	5.9	0.4	9.5	8.6	32.9	42.4
9	γ -Al ₂ O ₃	97.7	27.2	3.6	3.4	1.6	9.5	30.1	35.1
10	$Fe_{4.8}/\gamma$ -Al ₂ O ₃	98.7	35.2	10.4	3.6	5.4	16.1	45.0	57.7
11	$Fe_{9.7}/\gamma$ -Al ₂ O ₃	98.2	37.1	10.5	4.1	5.9	22.4	46.7	66.2
12	$Fe_{29.7}/\gamma$ - Al_2O_3	99.8	40.1	11.1	3.6	8.4	25.3	51.0	73.8

Reaction conditions: catalyst dosage 15 ml, reaction temperature 475 °C, atmospheric pressure, 20 wt% glycerol aqueous solution 0.25 mL/min, NH₃ 70 mL/min, time on stream 2-4 h.

^a Pyridine and 3-picoline were both found in the products of these entries.

^b Total yield of acetonitrile and propionitrile.

Table 2
Performances of catalysts doped with alkali or alkaline earth metals.

Entry	Catalyst	Conversion (%)	Selectivity	/ (%)		Yield ^a (%)	Carbon balance (%)		
			MeCN	EtCN	C_2H_4	C_3H_6	CO ₂		
1	$K_{0.2}/\gamma$ -Al ₂ O ₃	99.6	26.4	3.6	3.2	2.2	6.0	29.9	31.6
2	$Fe_{19.9}Li_{0.2}/\gamma - Al_2O_3$	99.3	36.0	11.4	3.3	10.6	18.9	47.1	67.1
3	$Fe_{19.4}Na_{0.2}/\gamma - Al_2O_3$	99.6	39.4	11.7	4.8	9.0	19.1	50.9	69.2
4	$Fe_{19.6}K_{0.1}/\gamma - Al_2O_3$	99.1	40.3	10.2	4.7	11.4	23.2	50.1	74.8
5	$Fe_{19.2}K_{0.2}/\gamma - Al_2O_3$	99.6	41.7	11.7	4.4	13.0	20.4	53.1	75.8
6	$Fe_{19.3}K_{0.3}/\gamma - Al_2O_3$	98.8	40.9	11.6	2.8	12.5	16.5	51.8	69.6
7	$Fe_{19.7}Mg_{0.2}/\gamma - Al_2O_3$	99.5	38.2	11.6	3.7	12.2	19.9	49.5	71.6
8	$Fe_{19.5}Ca_{0.2}/\gamma - Al_2O_3$	99.6	36.6	10.8	3.1	10.3	20.7	47.3	68.4
9	$Fe_{19.0}Sr_{0.2}/\gamma$ -Al ₂ O ₃	99.9	35.5	11.6	4.6	11.0	22.0	47.0	71.3

Reaction conditions: catalyst dosage 15 mL, reaction temperature 475 °C, atmospheric pressure, 20 wt% glycerol aqueous solution 0.25 mL/min, NH₃ 70 mL/min, time on stream 2–4 h.

^a Total yield of acetonitrile and propionitrile.

sult in further improvement of the total yield of nitriles (Table 2, entries, 4–6).

Doping bare alumina with 0.2% potassium did not improve the performance of γ -Al₂O₃ (Table 1, entry 9 and Table 2, entry 1), which indicates that the doping of potassium had some effect on the active species associated with Fe to improve the performance of the catalyst.

3.2. Performance of $Fe_{19,2}K_{0,2}/\gamma$ -Al₂O₃ under different reaction conditions

Initially, the reaction was run at 365 °C, which is a favourable temperature for the formation of acrolein [17,38–40]. However, very low selectivity towards propionitrile and acetonitrile was achieved due to the formation of other by-products, including methylamine, allyl alcohol and other unidentified compounds. Our previous work [31,34] indicated that reaction temperatures

higher than 400 °C were required to ensure the synthesis of nitriles in high yield from the amination of alcohols or styrene oxide. Therefore, the influence of the reaction temperature on the performance of the catalyst $Fe_{19,2}K_{0,2}/\gamma$ -Al₂O₃ was investigated in the temperature range of 425-550 °C under atmospheric ammonia pressure, which was maintained with a molar ratio of ammonia to glycerol of 6:1 and a GHSV of 1338 h⁻¹. The results shown in Table 3 indicated that the conversion of glycerol was almost quantitative under at all temperatures. A decreasing trend of the selectivity towards propionitrile was observed with an increase in temperature. However, the acetonitrile yield increased with an increase in the temperature from 425 to 525 °C and reached a maximum of 47.1% at 525 °C; a total yield of 56.2% of nitriles was obtained in this case (Table 3, entry 5). Above that temperature, the yield decreased with increasing temperature. The yields of ethylene and carbon dioxide increased with an increase in temperature. In contrast, the selectivity towards propylene decreased with an Table 3

Entry	Temperature (°C)	Conversion (%)	Selectivity (%)					Yield ^a (%)	Carbon balance (%)
			MeCN	EtCN	C_2H_4	C_3H_6	CO ₂		
1	425	99.3	34.5	12.8	0.1	1.2	16.5	46.9	53.6
2	450	98.3	34.6	13.4	2.5	16.9	18.1	47.2	73.1
3	475	99.6	41.7	11.7	4.4	13.0	20.4	53.1	75.8
4	500	100	42.5	10.6	5.4	11.9	21.3	53.1	75.7
5	525	99.7	47.1	9.3	6.6	6.4	25.1	56.2	76.5
6	550	99.4	43.0	7.3	8.5	2.1	27.0	50.0	70.8

Effect of the temperature on the performance of the $Fe_{19,2}K_{0,2}/\gamma$ -Al₂O₃ catalyst.

Reaction conditions: atmospheric pressure, ammonia/glycerol molar ratio 6:1, GHSV 1338 h⁻¹, time on stream 2-4 h.

^a Total yield of acetonitrile and propionitrile.

increase in temperature. Overall, high temperature favoured the formation of the products derived from the pyrolysis of glycerol, but low temperature favoured the formation of propionitrile in the experimental temperature range.

The influence of the molar ratio of ammonia to glycerol on the reaction was investigated under atmospheric ammonia pressure and a GHSV of 1338 h⁻¹ at 525 °C. The results are presented in Table 4. As shown in the table, the yields of both propionitrile and acetonitrile increased with an increase in the molar ratio of ammonia to glycerol from 4:1 to 8:1, and they reached their maxima of 10.5% and 47.9% at a ratio of 8:1 (Table 4, entry 3). The yields then decreased gradually with further increases in the molar ratio of ammonia to glycerol. The possible reason may be that appropriate excess ammonia can promote the condensation of acrolein and acetaldehyde with ammonia to form imines, which are the key intermediates in the formation of nitriles. However, when the excess ammonia was too large, for example, when the molar ratio of ammonia to glycerol was higher than 10, the ammonia could be adsorbed on the acid centres of the catalyst, weakening the acidity of the catalyst and impeding the condensation of aldehydes with ammonia to form imines. Additionally, a decreasing trend in the selectivity towards propylene was observed with the increase in the molar ratio of ammonia to glycerol.

The effect of the molar ratio of ammonia to glycerol was investigated under different K content. Similar results to those of 0.2% of K content were obtained. The detailed results are given in Supplementary material.

GHSV is also an important parameter that is generally considered for a catalytic reaction occurring in a fixed-bed reactor. Therefore, the influence of GHSV on the catalytic performance was investigated under atmospheric ammonia pressure and a molar ratio of ammonia to glycerol of 8:1 at 525 °C. The results are shown in Table 5. The reaction was run first at a very large GHSV to maintain a low conversion of glycerol to elucidate the reaction pathways (Table 5, entries 1 and 2). The composition of the reaction mixture was analysed by GC–MS, several intermediates including methanol, acetaldehyde, ethanol, allyl alcohol, 1-propanol and Nethyl methylenimine were detected. The GHSV was then lowered to an appropriate range to increase the conversion of glycerol and the selectivity of the target products. The results indicated that the conversion of glycerol stayed close to 100% as the GHSV was varied from 1722 to 918 h⁻¹. The selectivity of acetonitrile had a slight increase with the decrease in GHSV from 1722 to 1146 h⁻¹ (Table 5, entries 4–7) and then decreased after further reducing GHSV from 1146 to 918 h⁻¹. The selectivity of propionitrile reached its maximum of 11.9% at the GHSV of 1545 h⁻¹ (Table 5, entries 7, 8). Meanwhile, the selectivity of propylene decreased with the decrease in GHSV. A low GHSV indicates a long residence time of the reactants on the catalyst. Therefore, an appropriate GHSV favoured the formation of acetonitrile from glycerol decomposition and the tandem reactions that followed; however, if the GHSV was too low, the intermediates derived from glycerol underwent deep decomposition into small molecules, such as ethylene, H₂, and CO₂.

3.3. Lifetime and regeneration of the $Fe_{19,2}K_{0,2}/\gamma$ -Al₂O₃ catalyst

The optimised conditions-catalyst $Fe_{19,2}K_{0,2}/\gamma$ -Al₂O₃ 15 ml (7.1 g), molar ratio of NH₃ to glycerol 8:1, atmospheric pressure, reaction temperature of 525°C, and GHSV of 1338 h⁻¹-were determined from the investigation of the parameters. The lifetime under the optimised conditions and the regeneration of $Fe_{19,2}K_{0,2}/\gamma$ -Al₂O₃ were then investigated. The results are shown in Fig. 1. The conversion of glycerol was always higher than 99%; however, the selectivity towards total nitriles decreased with the amount of time that the catalyst was on the stream. The selectivity towards total nitriles dropped from 58.4% to 51.3% with the catalyst on stream from 4 h to 16 h. The regeneration of the catalyst was performed by calcination in air at 550 °C for 6 h, and the reaction was run again using the regenerated catalyst. Though the amorphous substances were removed by calcination, as revealed by TEM, the performance of the catalyst was not recovered. The selectivity towards total nitriles was lower than before the regeneration of the catalyst. The reasons leading to deactivation of the catalyst will be discussed in the characterisation.

Under the optimised conditions, the converted amount of glycerol over 1 g of catalyst was 0.42 g h^{-1} , corresponding to 0.089 g h^{-1} of acetonitrile and 0.027 g h^{-1} of propionitrile received

Table 4

Effect of the molar ratio of ammonia to glycerol on the performance of the $Fe_{19.2}K_{0.2}/\gamma$ -Al₂O₃ catalyst.

Entry	Ammonia/glycerol	Conversion (%)	Selectivity	ı (%)			Yield ^a (%)	Carbon balance (%)	
			MeCN	EtCN	C_2H_4	C_3H_6	CO ₂		
1	4:1	99.7	41.4	8.0	5.7	4.8	24.8	49.4	69.1
2	6:1	99.7	47.1	9.3	6.6	6.3	25.1	56.4	76.5
3	8:1	100	47.9	10.5	5.2	4.1	25.6	58.4	75.7
4	10:1	99.7	47.2	9.8	6.6	3.8	26.4	56.9	75.9
5	12:1	99.9	46.4	9.0	7.3	2.9	26.5	55.4	74.3

Reaction conditions: atmospheric pressure, reaction temperature 525 °C, GHSV 1338 h⁻¹, time on stream 2-4 h.

^a Total yield of acetonitrile and propionitrile.

Table 5 Effect of GHSV on the performance of the $Fe_{19.2}K_{0.2}/\gamma$ -Al₂O₃ catalyst.

Entry	$GHSV(h^{-1})$	Conversion (%)	Selectivity	r (%)		Yield ^a (%)	Carbon balance (%)		
			MeCN	EtCN	C_2H_4	C_3H_6	CO ₂		
1	13,739	69.3	13.9	5.4	0.7	0.4	15.2	13.4	30.7
2	8017	76.7	24.9	7.1	0.9	1.1	16.3	24.5	41.7
3	4014	93.3	37.5	9.6	2.5	2.6	16.6	43.9	55.5
4	1722	100	45.8	10.9	4.6	4.9	19.9	56.7	69.3
5	1545	99.9	46.1	11.9	4.3	4.7	24.8	58.0	75.0
6	1338	100	47.9	10.6	5.2	4.1	25.6	58.5	75.7
7	1146	99.9	47.9	9.8	5.5	3.8	27.8	57.7	77.1
8	918	99.9	45.4	8.6	6.8	2.2	26.9	54.0	72. 6

Reaction conditions: atmospheric pressure, reaction temperature 525 °C, ammonia/glycerol 8:1, time on stream 2-4 h.

^a Total yield of acetonitrile and propionitrile.



Fig. 1. The glycerol conversion and the yield of total nitriles as functions of reaction time.

in the first 4 h. In this case the conversion ammonia was about 12%. Throughout the process, the converted amount of glycerol was maintained, but the respective yields of acetonitrile and propionitrile dropped with time and reached approximately 0.078 g h^{-1} and 0.021 g h^{-1} at the period of 14–16 h of catalyst on stream.

3.4. Pathways for product generation

To elucidate the pathways for the catalytic conversion of glycerol over the $Fe_{19.2}K_{0.2}/\gamma-Al_2O_3$ catalyst, the reaction was run under low glycerol conversion. Apart from the four major products (propionitrile, acetonitrile, propylene and ethylene), methanol, acetaldehyde, ethanol, allyl alcohol, 1-propanol and N-ethyl methylenimine were also detected by GC–MS. Moreover, Hutchings [22] and others [11] have disclosed that hydroxyacetone, ethanol, propanal, allyl alcohol are by-products in the acid-catalysed double dehydration of glycerol to acrolein. Therefore, ethanol, 1-propanol, propionaldehyde, allyl alcohol, the mixture of formaldehyde and acetaldehyde, and hydroxyacetone were used as reactants under the same operation conditions performed for the catalytic conversion of glycerol over the $Fe_{19.2}K_{0.2}/\gamma$ -Al₂O₃ catalyst in order to investigate the reaction pathway. The results are shown in Table 6.

The main products obtained when ethanol was employed as reactant (Table 6, entry 1) were acetonitrile, ethylene and CO₂. The acetonitrile is formed through the amination–dehydrogenation process [28,31], and ethylene is obtained from the dehydration of ethanol. The CO₂ is generated from the decomposition of the intermediates derived from ethanol in the catalytic process.

Propionitrile, acetonitrile, propylene and CO_2 were the major products during catalytic conversion of 1-propanol over the $Fe_{19,2}K_{0,2}/\gamma$ -Al₂O₃ catalyst (Table 6, entry 2). When allyl alcohol was employed as reactant (Table 6, entry 4), the main products obtained were also propionitrile, acetonitrile, propylene and CO₂. In the case of propionaldehyde as reactant, propionitrile, acetonitrile and CO₂ as main products were obtained, and ethylene and propylene were also detected (Table 6, entry 3). These results suggest that 1-propanol, allyl alcohol and propionaldehyde as intermediates may be present in the catalytic conversion of glycerol.

When the mixture of formaldehyde and acetaldehyde was fed as reactant, acetonitrile as main product was obtained, and ethylene and propylene were also received (Table 6, entry 5). High yield of CO_2 was also obtained, which is mainly derived from the decomposition of formaldehyde over the catalyst. The propylene is derived from 3-hydroxypropanal formed from aldol reaction of formaldehyde and acetaldehyde. Generally, aldol reaction is reversible. These results confirm that acetaldehyde and 3-hydroxypropanal are also intermediates in the catalytic conversion of glycerol.

When hydroxyacetone was employed as reactant, the main products obtained were acetonitrile, propionaldehyde and CO₂, and ethylene and propylene were also observed (Table 6, entry 6).

Taking into account the catalytic results stated in Table 6, and the mechanism proposed for the transformation of glycerol to acrolein and by-products in literature [11,22,41], we were able to propose pathways for glycerol conversion (Scheme 4).

During the catalytic amination of glycerol, dehydration reactions occurred on the acid sites, producing water and dehydrated compounds. Dehydrogenation reactions also occurred on the catalyst's active sites of hydrogenation-dehydrogenation, producing hydrogen and carbonyl compounds. Decarbonylation of the diketones from the dehydration or dehydrogenation of hydroxyl carbonyl compounds generated acetaldehyde, which condensed with ammonia to generate the intermediate ethyleneimine. Then, ethyleneimine was dehydrogenated to give acetonitrile. Meanwhile, acetaldehyde could also be hydrogenated to ethanol, which was further dehydrated to give ethylene. Acrolein was produced from the double dehydration of glycerol. Once acrolein was formed, there were two possible pathways to produce propionitrile from acrolein. In one path, acrolein condensed with ammonia to generate the intermediate imine. Then, the imine was dehydrogenated to give acrylonitrile and hydrogen. Lastly, the carbon-carbon double bond in the acrylonitrile molecule was hydrogenated with the hydrogen generated in situ to give propionitrile. In the other path, acrolein was first dehydrogenated to give propylaldehyde. Then, propylaldehyde condensed with ammonia, and dehydrogenation followed to give propionitrile. In the same way that ethylene was formed, propylaldehyde from the hydrogenation of acrolein was hydrogenated to propanol, which was further dehy-

Table 6
Catalytic amination results of speculated intermediates over the $Fe_{19,2}K_{0,2}/\gamma\text{-}Al_2O_3$ catalyst

Entry	Reactants	Conversion (%)	Selectivity (Selectivity (%) ^b			
			MeCN	EtCN	C_2H_4	C ₃ H ₆	CO ₂
1	Ethanol	100	25.9	-	16.6	-	27.2
2	1-Propanol	100	5.3	13.6	-	7.5	6.9
3	Propionaldehyde ^c	100	10.3	37.0	0.2	0.2	17.3
4	Allyl alcohol	100	19.3	23.9	-	11.8	8.5
5	Formaldehyde + Acetaldehyde ^a	100	61.0	-	5.5	1.2	61.6
6	Hydroxyacetone	100	34.4	13.4	1.0	0.3	17.7

Reaction conditions: catalyst Fe_{19.2}K_{0.2}/γ-Al₂O₃ dosage 15 mL, reaction temperature 525 °C, atmospheric pressure, ammonia/substrate 8:1, GHSV 1338 h⁻¹, time on stream 2– 4 h, aqueous solution of 20 wt% of intermediate.

^a Mixture of aqueous solutions of formaldehyde (10 wt%) and acetaldehyde (10.8 wt%), molar ratio of formaldehyde/acetaldehyde 1:1.4.

^b The selectivity of acetonitrile, propionitrile, ethylene and propylene is based on acetaldehyde, and the selectivity of carbon dioxide is based on formaldehyde in entry 5. ^c 10 wt% Aqueous solution.



Scheme 4. Possible formation pathways of the products during the catalytic amination of glycerol.

drated to give propylene. The unsaturated glycol or aldehyde species from the dehydration and dehydrogenation of glycerol and the imines from the condensation of aldehydes with ammonia underwent oligomerisation to generate oligomers, which finally transformed to carbon deposit.

Finally, steam cracking of glycerol and the intermediates may produce CO and H₂ under the reaction conditions over the catalyst as shown in Eq. (1), and then CO was converted into CO₂ and more H₂ was produced through water-gas-shift (WGS) reaction as shown in Eq. (2) [11].

$$C_x H_y O_z + (x - z) H_2 O \rightarrow x CO + (y/2 + x - z) H_2$$
 (1)

 $CO+H_2O\rightarrow CO_2+H_2$ (2)

3.5. Characterisation of the catalysts

The porous structure and specific surface areas of fresh Fe_{19.5}/ γ -Al₂O₃ and fresh, used, and regenerated $Fe_{19,2}K_{0,2}/\gamma$ -Al₂O₃ were analysed by N₂ adsorption-desorption. The adsorption-desorption isotherms are shown in Fig. 2. All of the samples displayed type IV isotherms, which is indicative of the existence of mesopores in the catalysts. In addition, the hysteretic loops of the samples are similar to the type H4, which is indicative of slit-like pores [42].

Table 7 presents the specific surface areas and the range of the pore structural parameters of the $Fe_{19.5}/\gamma$ -Al₂O₃ and the fresh, used and regenerated Fe_{19.2}K_{0.2}/\gamma-Al_2O_3. The fresh Fe_{19.2}K_{0.2}/\gamma-Al_2O_3 showed a slightly higher surface area compared to $Fe_{19.5}/\gamma$ -Al₂O₃. The observed slight increase in the specific surface area can be attributed to the fact that doping with potassium facilitates the high dispersion of the catalyst crystallites and, as a result, increased the BET surface of the iron oxide-based catalyst [43,44], which is one of the factors improving the performance of the catalyst. In fact, the mean pore diameter values for the catalysts decreased from 7.0 to 6.2 nm upon doping with 0.2 wt% potassium. The increase in the specific surface area as a result of doping with potassium can also be attributed to the creation of pores produced from the liberation of gaseous nitrogen oxides during the thermal



Fig. 2. Adsorption–desorption isotherms of the catalyst samples. (a) $Fe_{19.5}/\gamma$ -Al₂O₃, (b) $Fe_{19.2}K_{0.2}/\gamma$ -Al₂O₃ (used), (d) $Fe_{19.2}K_{0.2}/\gamma$ -Al₂O₃ (regenerated).

Table 7

Textural properties of catalysts.

$V^{a} (m^{2} g^{-1}) = V^{b} (cm^{3} g^{-1})$) $d_p^{c}(nm)$
0.32	7.0
0.31	6.2
0.32	7.5
0.26	6.7
	$\begin{array}{ccc} \overset{a}{=}(m^2g^{-1}) & V^b(cm^3g^{-1}) \\ & 0.32 \\ & 0.31 \\ & 0.32 \\ & 0.26 \end{array}$

^a BET surface area.

^b BJH cumulative desorption pore volume.

^c Mean pore diameter = 4 V/S_{BET}.

decomposition of KNO₃ during the thermal treatment of doped solid at 550 °C [45].

The pore size distributions of the catalyst samples are displayed in Fig. 3. The mesopores were mostly concentrated at 5.2 nm in $Fe_{19.5}/\gamma$ -Al₂O₃, whereas the pore size distributions of the fresh $Fe_{19,2}K_{0,2}/\gamma$ -Al₂O₃ were fairly narrow, with a maximum at approximately 4.0 nm, indicating a better dispersion after the doping with potassium. After the catalyst $Fe_{19,2}K_{0,2}/\gamma$ -Al₂O₃ was on stream for 4 h, the BET surface area decreased from 178 m²/g to 141 m²/g, corresponding to a decrease in the total selectivity of nitriles of the catalyst in the catalytic run, which can be ascribed to the deposition of carbon and other nonvolatile materials on the pores of the catalyst hindering the contact of reactants with active sites. However, the pore volume and the mean pore diameter of the sample of the used catalyst increased to some degree compared to those of the sample of the fresh catalyst, which can be attributed to the pore size distributions changes of the catalyst before and after use. After the catalyst was used, the pores with small diameters were blocked due to the deposition of carbon and other non-volatile materials, corresponding to the shift in the pore size distributions towards large ones. As shown in Fig. 3, the maximum of the pore size distribution changes from 4.0 nm to 5.2 nm. After the used catalyst was calcined at 550 °C in air for 6 h, the maximum of the pore size distributions changed from 5.2 nm to 4.5 nm. However, the surface areas of the sample of the regenerated catalyst did not increase, indicating the agglomeration of iron oxides in the regeneration process, as confirmed by the TEM analysis.

The deposition of carbon was further confirmed by TEM images. Representative TEM images of the samples of fresh $Fe_{19.5}/\gamma$ -Al₂O₃ and fresh, used, and regenerated $Fe_{19.2}K_{0.2}/\gamma$ -Al₂O₃ are shown in



Fig. 3. Pore size distribution curves as a function of pore diameter. (a) Fe_{19.5}/ γ -Al₂O₃, (b) Fe_{19.2}K_{0.2}/ γ -Al₂O₃ (fresh), (c) Fe_{19.2}K_{0.2}/ γ -Al₂O₃ (used), (d) Fe_{19.2}K_{0.2}/ γ -Al₂O₃ (regenerated).

Fig. 4. The image of the sample of fresh $Fe_{19.5}/\gamma$ -Al₂O₃ shows nanoparticles with an average diameter of 4–8 nm (Fig. 4a). The particle size displayed in the image of the fresh $Fe_{19.2}K_{0.2}/\gamma$ -Al₂O₃ is a diameter of 2–5 nm, smaller than that of fresh $Fe_{19.5}/\gamma$ -Al₂O₃. It is also well dispersed, which is attributed to the doping of potassium into $Fe_{19.5}/\gamma$ -Al₂O₃. The particle size displayed in the image of the regenerated $Fe_{19.2}K_{0.2}/\gamma$ -Al₂O₃ is a diameter of 5–10 nm, larger than that of the fresh catalyst, indicating that agglomeration of iron oxides occurred in the regeneration process, which is consistent with the N₂ adsorption–desorption analysis.

Amorphous substances covering the surface of the catalyst can be seen by comparing the image of the used $Fe_{19,2}K_{0,2}/\gamma$ -Al₂O₃ with that of the fresh catalyst, which shows active species particles that are not clearly displayed. No amorphous substances were observed in the TEM image of the regenerated $Fe_{19,2}K_{0,2}/\gamma$ -Al₂O₃, which indicated that the carbonaceous deposits can be removed by calcination at 550 °C for 6 h. However, the catalytic performance of the catalyst was not recovered, as shown in Fig. 1. The TEM and N₂ adsorption-desorption analysis characterisation in combination with the catalytic test results indicated that the formation of carbon deposits is not the only cause of the deactivation of the catalyst during the catalytic run, which is different from that of the zinc-based catalysts for the amination of allyl alcohol to propionitrile reported by us [34]. Agglomeration of iron oxides during the catalytic run or in the regeneration process may be another cause of the deactivation of the catalyst.

The EDX analysis revealed the presence of Fe, K, Al and O in the samples of the fresh, used, and regenerated catalyst. The elemental carbon detected in the used sample of the catalyst can be attributed to the carbon deposition in the catalytic run, and the contamination of the sample in the TEM analysis.

The amount of carbonaceous deposits on the catalyst was determined by TG-DSC and the results are shown in Fig. 5. A total weight loss of 10% mainly taking place in the temperature range of 270 °C to 500 °C was found, which indicated that the carbonaceous deposits were removed by combustion. The carbonaceous deposits account for some of the poor carbon balances in the catalytic conversion of glycerol over the catalyst.

Fig. 6 shows the XRD patterns of γ -Al₂O₃, Fe_{19.5}/ γ -Al₂O₃ and fresh, used, and regenerated Fe_{19.2}K_{0.2}/ γ -Al₂O₃. For all samples of the catalysts, the peaks representing the support γ -Al₂O₃ were found. Both the patterns of the samples of the fresh Fe_{19.5}/ γ -Al₂O₃ and Fe_{19.2}K_{0.2}/ γ -Al₂O₃ have an Fe₂O₃ crystalline phase. However, no Fe₂O₃ crystalline phase was observed in the patterns of the samples of the used Fe_{19.2}K_{0.2}/ γ -Al₂O₃. Instead, an Fe₃O₄ crystalline



Fig. 4. TEM micrographs of the catalyst samples and EDX spectra at points 1, 2, 3. (a) $Fe_{19.5}/\gamma$ - Al_2O_3 , (b) $Fe_{19.2}K_{0.2}/\gamma$ - Al_2O_3 (fresh), (c) $Fe_{19.2}K_{0.2}/\gamma$ - Al_2O_3 (used), (d) $Fe_{19.2}K_{0.2}/\gamma$ - Al_2O_3 (regenerated), (e) EDX spectra at points 1, 2 and 3. The carbon contents are 11.2%, 24.6% and 14.8% at points 1, 2 and 3, respectively.



Fig. 5. TG-DSC analysis of the used $Fe_{19,2}K_{0,2}/\gamma$ -Al₂O₃ catalyst.

phase was displayed. The results indicated that the Fe_2O_3 was transformed to Fe_3O_4 during the catalytic run. The transformation of the Fe_2O_3 crystalline phase to the Fe_3O_4 crystalline phase is due to the reduction of Fe_2O_3 by the in situ-generated H_2 as shown in Eq. (3) [46].

$$3Fe_2O_3 + H_2 \to 2Fe_3O_4 + H_2O \tag{3}$$

The patterns of the sample of the regenerated Fe_{19.2}K_{0.2}/ γ -Al₂O₃ were almost the same as those of the sample of the used catalyst, except for a few weak peaks of Fe₂O₃, which indicated that only a part of the Fe₂O₃ crystalline phase was recovered by calcination at 550 °C in the air for 6 h, even though the carbon deposits were removed by this process. These results revealed that Fe₂O₃ was one of the dehydrogenation–hydrogenation active species of the catalyst and that the deactivation of the catalyst was in part due to the transformation of Fe₂O₃ to Fe₃O₄ by H₂ reduction in the catalytic run.

The average diameters of the Fe₂O₃ crystallites in the Fe_{19.5}/ γ -Al₂O₃ and fresh Fe_{19.2}K_{0.2}/ γ -Al₂O₃ were not calculated by using



Fig. 6. XRD patterns of the catalyst samples. (a) γ -Al₂O₃, (b) Fe_{19.5}/ γ -Al₂O₃, (c) Fe_{19.2}K_{0.2}/ γ -Al₂O₃ (fresh), (d) Fe_{19.2}K_{0.2}/ γ -Al₂O₃ (used), (e) Fe_{19.2}K_{0.2}/ γ -Al₂O₃ (regenerated).

Scherrer formula due to poor crystallinity of Fe_2O_3 crystallites. Because of agglomeration of iron oxides during the catalytic run or in the regeneration process as revealed by the TEM analysis, the crystallinity of the iron oxide crystallites was improved, and the average diameters of iron oxide crystallites in the used and regenerated $Fe_{19.2}K_{0.2}/\gamma$ -Al₂O₃ can be calculated by using the Scherrer formula. The average diameters of the iron oxide crystallites are 19.5 nm and 23.3 nm, respectively, larger than those observed from TEM images. The difference can be attributed to the still low crystallinity of iron oxide crystallites in the used and regenerated catalyst.

The surface compositions of the samples of fresh, used, and regenerated $Fe_{19.2}K_{0.2}/\gamma$ -Al₂O₃ were determined by XPS. The full spectrum is presented in the Supplementary material. The resulting XPS Fe 2p peak was curve-fitted as shown in Fig. 7. Due to broader, less intense peak structure in the $2p_{1/2}$ region and to errors that build up in higher-binding energy regions, concentration analysis is based on the Fe main $2p_{3/2}$ peak intensities only.

For the fresh sample, the spectrum can be successfully fitted to two main peaks and a satellite peak at 715.2 eV. The binding energy peaks at 710.9 eV and 712.9 eV are attributed to the Fe³⁺ species, respectively [47]. No peak binding energy peak attributed to Fe²⁺ is appeared. These confirm further that Fe₂O₃ is the dehydrogenation–hydrogenation active species in the catalyst Fe_{19.2}K_{0.2}/ γ -Al₂O₃.

For the sample of the used catalyst, the spectrum is fitted to three main peaks and two satellite peaks. The binding energy peaks at 710.9 eV and 712.3 eV and the satellite peak at 713.9 eV are attributed to the Fe^{3+} species [47]. The lowest binding energy peak at 709.3 eV attributed to the Fe^{2+} , with a corresponding satellite at 715.8 eV [48]. The mean relative areas of each constituent peak assigned to Fe^{2+} and Fe^{3+} were calculated, and the atomic ratio of Fe^{2+} to Fe^{3+} was 1:2.2. Because stoichiometric Fe_3O_4 can also be expressed as $FeO\cdotFe_2O_3$, the $Fe^{2+}:Fe^{3+}$ ratio should be 1:2. The results indicated that Fe_2O_3 was almost completely reduced to Fe_3O_4 by the in situ-generated H₂, which is consistent with the XRD analysis.

For the regenerated sample, the spectrum is also fitted to two main peaks and a satellite peak at 714.4 eV. The binding energy peaks at 710.4 eV and 712.2 eV are attributed to the Fe^{3+} species, respectively [47], no binding energy peak assigned to Fe^{2+} is observed. The results indicated that the Fe_3O_4 on the surface of the



Fig. 7. Fe 2p XPS spectra of the catalyst samples. (a) $Fe_{19,2}K_{0,2}/\gamma$ -Al₂O₃ (fresh), (b) $Fe_{19,2}K_{0,2}/\gamma$ -Al₂O₃ (used), (c) $Fe_{19,2}K_{0,2}/\gamma$ -Al₂O₃ (used), (c) $Fe_{19,2}K_{0,2}/\gamma$ -Al₂O₃ (regenerated).

Table 8	
Surface and bulk elemental compositions of the samples of the Fe _{19.2} K _{0.2} / γ -Al ₂ O ₃ cata	lyst.

Methods	Samples	C (%)	0 (%)	Al (%)	Fe (%)	Fe: Al ^c
XPS ^a	Fresh Used Regenerated	45.4 59.2 48.0	39.2 29.2 30.0	12.1 8.6 17.6	3.3 2.2 4.4	0.27 0.26 0.25
ICP ^b	Fresh Regenerated			42.6 42.7	19.2 19.1	0.22 0.22

^a Atomic%.

^b Mass%.

^c Molar ratio.



Fig. 8. IR spectra of pyridine adsorbed on the catalysts. (a) $Fe_{19.5}/\gamma-Al_2O_3$, (b) $Fe_{19.2}K_{0.2}/\gamma-Al_2O_3$ (fresh), (c) $Fe_{19.2}K_{0.2}/\gamma-Al_2O_3$ (used), (d) $Fe_{19.2}K_{0.2}/\gamma-Al_2O_3$ (regenerated).

used catalyst was completely converted to Fe_2O_3 after calcination at 550 °C in the air for 6 h. However, the Fe_3O_4 in the bulk was remained, that is why only weak peaks of Fe_2O_3 , but strong peaks of Fe_3O_4 were observed in the XRD patterns of the regenerated sample.

Table 8 presents the surface and bulk elemental compositions of the samples of the fresh, used and regenerated Fe_{19.2}K_{0.2}/ γ -Al₂O₃ catalyst from the XPS and ICP analysis. It revealed that the Fe:Al in the bulk is lower than that on the surface, indicating migration of Fe from bulk to surface in the calcination during the preparation process of the catalyst. It can also be seen that the molar ratio of Fe to Al in the bulk remained constant in the catalytic run and regeneration process, and the value on the surface decreased slightly, which indicated that the catalyst was stable and no further migration of Fe from bulk to surface took place in the catalytic run and regeneration process.

Fig. 8 shows the IR spectra of absorbed pyridine of the Fe_{19.2}K_{0.2}/ γ -Al₂O₃ and fresh, used and regenerated Fe_{19.2}K_{0.2}/ γ -Al₂O₃ catalyst samples in the region 1700–1300 cm⁻¹. Two peaks at 1545 cm⁻¹ and 1450 cm⁻¹ are attributed to the characteristic absorptions of pyridine adsorbed on the Brønsted and Lewis acid centres of the catalyst respectively [49–51]. The spectra show that both Fe_{19.5}/ γ -Al₂O₃ and Fe_{19.2}K_{0.2}/ γ -Al₂O₃ have Lewis acidity but weak Brønsted acidity. The doping of a small amount of potassium had no obvious effect on the acidity of the catalyst. The acid centres provide the catalyst with the ability to convert glycerol to acrolein by dehydration. The peaks at 1545 cm⁻¹ and 1450 cm⁻¹ in the spectrum of the used catalyst were almost destroyed and then recovered after regeneration, as seen by comparing the spectra of the fresh, used and regenerated samples of Fe_{19.2}K_{0.2}/ γ -Al₂O₃.

The significant changing of the spectrum of the used catalyst sample compared with that of the fresh catalyst indicated that some substances deposited on the surface of the catalyst in the catalytic run. However, the peaks at 1545 cm^{-1} and 1450 cm^{-1} are still visible by careful observation of the spectrum, indicating that acid sites are present in the catalyst. Therefore, the dehydration of glycerol to the intermediates is still feasible. Meanwhile, the deposited substances, as confirmed by TEM, also masked the active species Fe₂O₃, blocking the dehydrogenation of imine to nitriles to some degree, which is one of the reasons leading to a decrease in the selectivity towards nitriles. Although the deposited substances were removed by calcination, the performance of the catalyst was not recovered.

From the characterisation results of XRD, XPS and IR spectra of adsorbed pyridine, as well as the catalytic performance of the catalyst shown in Fig. 1, it can be concluded that both Fe_2O_3 and Fe_3O_4 can act as dehydrogenation–hydrogenation active species in the amination of glycerol to nitriles, but the activity of Fe_3O_4 is lower than that of Fe_2O_3 . It can also be concluded that the failure to recover the performance of the catalyst is due to the agglomeration of Fe_2O_3 and Fe_3O_4 phases in the catalytic run and the regeneration process in view of the TEM analysis.

4. Conclusion

An $Fe_{19.2}K_{0.2}/\gamma$ -Al₂O₃ catalyst was prepared and showed activity for the amination of glycerol to propionitrile and acetonitrile. The parameters that affected the catalyst performance were studied thoroughly, and an optimised process for synthesising nitriles from glycerol and ammonia over the catalyst was obtained. Under the optimised conditions, the total yield of propionitrile and acetonitrile was higher than 58%. The characterisation results indicated that the dehydrogenation reaction mainly occurred on the Lewis acid sites and that Fe₂O₃ is the main active species for the dehydrogenation of intermediate imines to nitriles and carbon-carbon double hydrogenation. Doping with 0.2% potassium to Fe_{19.5}/ γ -Al₂O₃ decreased the size of the Fe₂O₃ crystallites, which favoured the dehydrogenation of imines to nitriles and carbon-carbon double hydrogenation. The characterisation results revealed that the catalyst deactivation was mainly caused by carbon deposition on the catalyst and the reduction of Fe₂O₃ to Fe₃O₄ during the catalytic run. Meanwhile, agglomeration of the Fe₂O₃ and Fe₃O₄ phases during the catalytic run and regeneration process was the cause of the failed performance recovery of the catalyst by calcination.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/i.icat.2014.02.014.

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