



# Physicochemical attributes of oxide supported Mo<sub>2</sub>N catalysts synthesised via sulphide nitridation

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## Abstract

This study deals with the preparation and characterisation of supported Mo<sub>2</sub>N catalysts from the temperature programmed NH<sub>3</sub> nitridation of the precursor sulphides obtained via precipitation from homogeneous solution. Whilst nitridation temperature, H<sub>2</sub>:NH<sub>3</sub> ratio and reaction time were found to be important determinants of the BET surface area, chemisorptive parameters, acid site strength, density and surface spectroscopic features were also influenced by support-type. Among the four supports (alumina, silica, zirconia and titania) used, the 12% Mo<sub>2</sub>N/Al<sub>2</sub>O<sub>3</sub> catalyst yielded the highest BET surface area (200 m<sup>2</sup> g<sup>-1</sup>) while the ZrO<sub>2</sub>-supported sample exhibited the best dispersion (13%) and lowest particle size at 10 nm. The heat of desorption for NH<sub>3</sub> based on TPD runs lies between -150 and -130 kJ mol<sup>-1</sup> for all catalysts and is comparable to those found for Pt supported on similar oxides. In spite of the high H<sub>2</sub> uptake on the Mo<sub>2</sub>N/ZrO<sub>2</sub> catalyst, based on CO hydrogenation reaction, the turnover frequency decreased in the order: alumina > silica > zirconia > titania.

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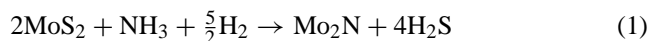
**Keywords:** Molybdenum nitride; Fischer Tropsch reaction; Alumina; Zirconia; Silica; Titania

## 1. Introduction

Early transition metal nitrides constitute an important class of new catalytic materials which possess high activity for a variety of petrochemical reactions—hydrodesulphurisation, hydrodenitrogenation, hydrogenation, hydrogenolysis, dehydrogenation and isomerisation [1–4], due to their electronic resemblance to more expensive noble metals like Pt and Pd [5]. In particular, they offer excellent anticoking and sulphur-resistance characteristics and may therefore be used as multifunctional catalysts in the petroleum refining industry. They are commonly produced by temperature programmed reaction between the transition metal oxide and a nitrogen-containing agent such as N<sub>2</sub> or NH<sub>3</sub>. The resulting metal nitrides therefore have relatively poor porosity and low surface areas. Development of novel techniques for the preparation of high surface area metal nitrides has therefore attracted substantial research efforts [6]. Previous studies

[7,8] in our laboratory have shown that high surface area metal sulphides may be obtained via precipitation from homogeneous solution (PFHS) on to an appropriate support. It is therefore conceivable that the metal sulphide may be employed as a precursor for the synthesis of the supported metal nitride since the temperature range for the nitridation process is similar to that for sulphidation.

In the present work, we report the preparation of Mo<sub>2</sub>N supported on various semi-conductor oxides, namely; silica, alumina, zirconia and titania in order to determine the influence of support-type on the physicochemical characteristics of the catalyst. The pertinent nitridation reaction is



O'Brien and co-workers [9] as well as Chen et al. [10] have reported the effect of several preparation variables such as temperature, duration of nitridation, nitriding gas composition, heating rate and source of materials (nitrogen and metals) on the attributes of the resulting metal nitride. Nitridation temperature will influence both the morphological properties of the catalyst and the extent of phase conversion from the sulphide to nitride. Furimsky [11] reported that

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nitridation between 773 and 1173 K yielded various Mo nitride species ( $\gamma$ -Mo<sub>2</sub>N and  $\beta$ -Mo<sub>2</sub>N<sub>0.78</sub> and even metallic Mo) with the  $\gamma$ -Mo<sub>2</sub>N species being the most favoured at low temperatures. Although pure NH<sub>3</sub> has been used when Mo oxide is the substrate, the addition of H<sub>2</sub> will be necessary to facilitate sulphide reduction as may be seen from Eq. (1). Thus, H<sub>2</sub>:NH<sub>3</sub> ratio will dictate the degree of reduction of the precursor before nitrogen dissolution in the Mo lattice. In order to provide a basis for quantitative optimisation, the effects of nitridation temperature, H<sub>2</sub>:NH<sub>3</sub> ratio and reaction time on Mo<sub>2</sub>N synthesis were investigated via a 2<sup>3</sup> factorial design in order to identify the ‘best’ conditions for catalyst preparation. The support influence was evaluated on the basis of BET area, chemisorption parameters, acid site density and strength. An assessment of the activity was also made using the CO hydrogenation reaction.

## 2. Experimental

### 2.1. Catalyst preparation

All chemicals were obtained from Aldrich (Sydney, Australia) with exception of zirconia supplied by Millenium Chemicals (Perth, Australia). Doubly distilled de-ionised water was used for preparing all solutions. The base MoS<sub>2</sub> was prepared on various supports (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and TiO<sub>2</sub>) using precipitation from homogeneous solution. This involved the intimate mixing of 0.1 M of (NH<sub>4</sub>)Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O with 1 g urea, 1 ml 0.75 M HNO<sub>3</sub> and 30 ml of thioacetamide with 0.7 g of the support in a 250 ml conical flask containing 10% (NH<sub>4</sub>)<sub>2</sub>S solution. The conical flask

was then placed in a continuous shaker water-bath maintained at 110 rpm and 363 K for 4 h. The resulting slurry was filtered, washed and dried at 393 K overnight. Nitridation was then carried out in the experimental set up shown in Fig. 1 by placing 0.7 g of the dried supported-MoS<sub>2</sub> between two layers of quartz wool in a quartz tube (i.d. = 6 mm), coaxial with a vertical tubular temperature programmable furnace. Brooks mass flow controllers were used to regulate the H<sub>2</sub> and NH<sub>3</sub> gas lines so that a total mixture of 100 ml min<sup>-1</sup> was passed downwards into the reactor (irrespective of the H<sub>2</sub>:NH<sub>3</sub> ratio, 1 or 5, used). A heating rate of 5 K min<sup>-1</sup> was employed to bring the reactor to the desired nitridation temperature (773–973 K) and maintained isothermally at that level for the reaction period (1 or 4 h). The samples were then cooled down in the nitriding gas and subsequently passivated in 1% O<sub>2</sub>/He mixture in view of the pyrophoric nature of the specimens. Eight catalysts were prepared using the conditions listed in Table 1.

### 2.2. Characterisation of catalyst samples

Physicochemical properties of the Mo nitride samples were determined in order to understand role of preparation conditions and support on the catalytic performance. BET surface area was measured using N<sub>2</sub> physisorption at 77 K on a Micromeritics Tristar 3000. H<sub>2</sub> uptake measurements were carried out at 373 K in a Micromeritics AutoChem 2910. The latter was also used to determine acid site strength and concentration based on NH<sub>3</sub>-temperature programmed desorption. Temperature programmed reduction (TPR) with hydrogen was performed on a ThermoCahn TGA 2121 at a heating rate of 2 K min<sup>-1</sup> up to 873 K. FT-IR spectra were

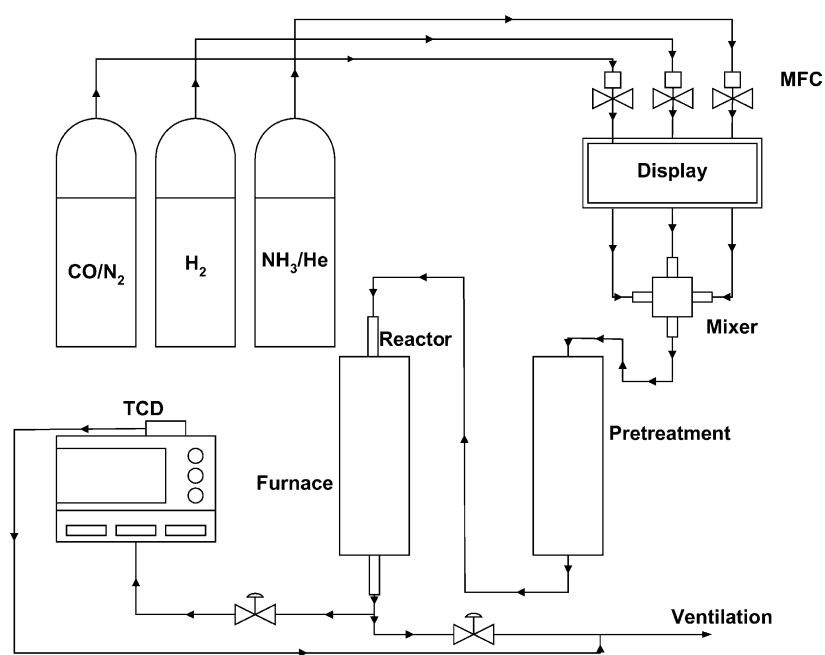


Fig. 1. Schematic diagram of experimental set up.

Table 1  
Yates' analysis on BET area of silica-supported Mo<sub>2</sub>N

Sample	Nitridation temp (K)	Ratio H <sub>2</sub> :NH <sub>3</sub>		Time (h)	Avg BET surface area (m <sup>2</sup> /g) ( <i>S</i> <sub>BET</sub> )	Degrees of freedom	Variance estimates	Effect ID	Calc. <i>F</i> -values
1	773	1	1	1	78.94	8	96.62	Average	
2	973	1	1	1	92.36	4	18.08	<i>T</i>	55.29
3	773	5	1	1	85.24	4	8.47	<i>C</i>	25.88
4	973	5	1	1	100.07	4	0.37	<i>TC</i>	1.15
5	773	1	1	4	88.12	4	14.94	<i>t</i>	45.62
6	973	1	1	4	110.12	4	3.96	<i>Tt</i>	12.09
7	773	5	1	4	98.02	4	1.47	<i>Ct</i>	4.49
8	973	5	1	4	120.12	4	-0.32	<i>TCt</i>	1

obtained from a Nicolet Nexus spectrophotometer scanning from 400 to 4000 cm<sup>-1</sup> with 100 scans performed for each sample, at a resolution of 4 cm<sup>-1</sup> with KBr as background.

For catalyst evaluation, the sample was cooled from the nitridation temperature, 973 K, to a reaction temperature of 573 K in the NH<sub>3</sub>/H<sub>2</sub> mixture before admitting a reactant mixture of H<sub>2</sub>:CO = 2 at a total flow rate of 30 ml min<sup>-1</sup> controlled and maintained by Brooks mass flow controller (5850 Series). Reactants were taken to 573 K in a preheater before entering the reactor/furnace assembly. Products (C<sub>1</sub>–C<sub>5</sub> hydrocarbons) were analysed by on-line TCD gas chromatograph (Shimadzu Model GC-8A).

### 3. Results and discussion

#### 3.1. BET surface area analysis

Table 1 shows the surface area of all eight silica supported catalysts prepared under different nitridation conditions. It is evident that nitridation temperature, H<sub>2</sub>:NH<sub>3</sub> ratio and reaction time all had positive effects on the surface area with the highest BET area (120.12 m<sup>2</sup> g<sup>-1</sup>) obtained at 973 K for treatment with H<sub>2</sub>:NH<sub>3</sub> = 5 for 4 h. The variance estimates provided in column 8 were calculated via Yates' analysis and indicated that the three-factor interaction, *TCt*, has the smallest variance. The sign of each variance is simply an indication of the direction of its contribution suggesting that increase in all the three-factors would improve the catalyst BET surface area. Computed *F*-values displayed in column 10 were compared with the tabulated *F*-values at 95% confidence level (6.39). This confirmed the statistical significance of *T*, *C* and *t* as well as the two-factor interaction between temperature and time, *Tt*. Thus, the data may be described by

$$S_{BET} = a_0 + a_1 X_T + a_2 X_C + a_3 X_t + a_4 X_T X_t \quad (2)$$

where

$$X_T = \frac{T - 773}{200}$$

$$X_C = \frac{C - 1}{4}$$

$$X_t = \frac{t - 1}{3}$$

Linear regression provides estimates of the model coefficients as  $a_0 = 77.85$ ,  $a_1 = 14.1$ ,  $a_2 = 8.47$ ,  $a_3 = 10.98$  and  $a_4 = 7.95$ . As a result of this statistical analysis, subsequent supported Mo<sub>2</sub>N catalysts were prepared using a nitriding gas mixture of H<sub>2</sub>:NH<sub>3</sub> = 5, at 973 K for 4 h. The contribution of the *Tt* factor interaction suggests that increasing the heating rate was also an important determinant of the catalyst surface area and indeed, increasing this variable beyond the 2 K min<sup>-1</sup> used in this study has the potential to further enhance BET area. Thus a heating rate of 5 K min<sup>-1</sup> was employed in subsequent catalyst preparations using other oxide supports. Fig. 2 reveals that the alumina-supported catalyst has the highest surface area (200 m<sup>2</sup> g<sup>-1</sup>) while titania catalyst has the lowest surface area of about 9 m<sup>2</sup> g<sup>-1</sup>. Colling et al. [12] had also reported a BET area of 193 m<sup>2</sup> g<sup>-1</sup> for Mo<sub>2</sub>N/alumina catalyst. Interestingly, the trend in surface area among this group of inorganic oxide supports is also similar to that obtained for Co–Mo oxide supported on the same material but prepared via conventional impregnation technique [13].

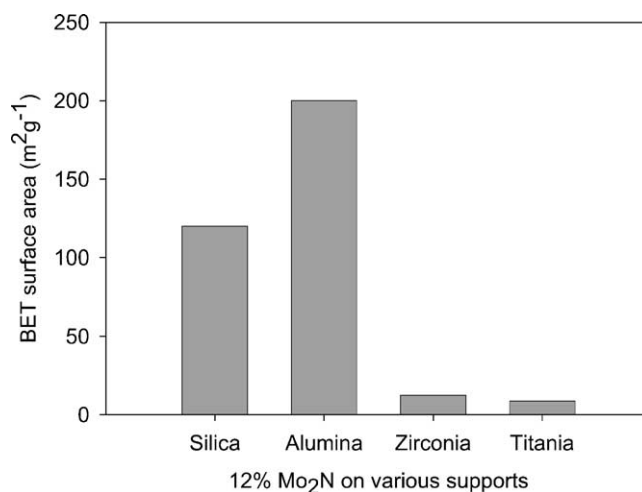


Fig. 2. BET area on all supports.

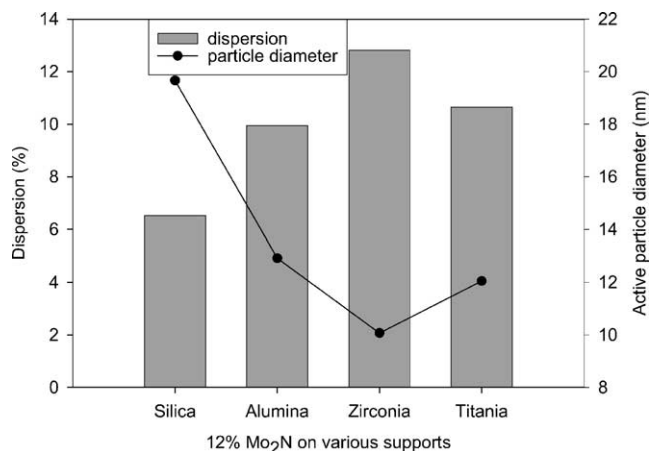


Fig. 3. H<sub>2</sub> chemisorption parameters.

### 3.2. H<sub>2</sub> chemisorption and temperature programmed reduction

Data for pulse H<sub>2</sub> chemisorption on all four supported catalysts may be seen on Fig. 3. The surface of Mo<sub>2</sub>N may contain metallic as well as acidic sites [14] which act as hydrogen activation centres, thus, H<sub>2</sub> uptake measurements may provide some indication of the catalytic effectiveness for hydrogenation reactions. It is evident that the PFHS method gave well-dispersed Mo nitride crystallites with the ZrO<sub>2</sub> catalyst yielding the best dispersion (12.81%) and the correspondingly lowest Mo<sub>2</sub>N crystallite size (10.07 nm) while the poorest, Mo<sub>2</sub>N/SiO<sub>2</sub> catalyst with 6.5% dispersion and 19.7 nm particles, is still comparable to those obtained by Zhang and co-workers [15]. Fig. 4 reveals that if the H<sub>2</sub> uptake surface area (between 30 m<sup>2</sup> g<sup>-1</sup> for silica to a maximum of 70 m<sup>2</sup> g<sup>-1</sup> for zirconia) was normalised with the BET surface area, it became apparent that less than 10% of the total surface area of the alumina and silica catalysts was available for hydrogen chemisorption while the zirconia and titania catalysts exhibited better surface H<sub>2</sub> adsorption capacity. Zhang et al. [15] also observed that only about 10%

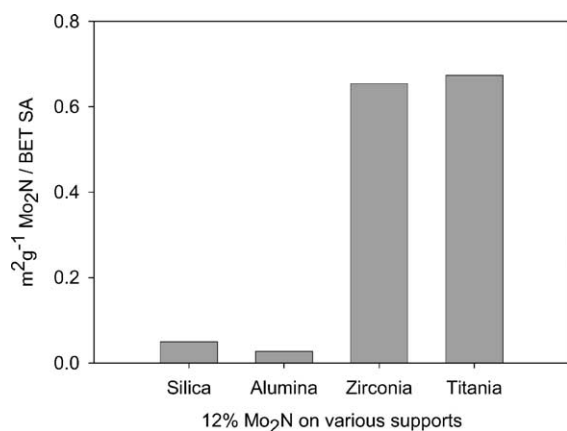


Fig. 4. Mo<sub>2</sub>N deposition efficiency.

of the surface Mo atoms were involved in H<sub>2</sub> activation on their alumina-supported Mo<sub>2</sub>N. Dissociative adsorption of H<sub>2</sub> presumably takes place on both surface—Mo atoms and the nitrogen-deficient patch of Mo—N present on the surface of the catalyst [16].

H<sub>2</sub> temperature programmed reduction up to 873 K was conducted on all four samples and the spectra are shown in Fig. 5(a–d). Large peaks observed below 473 K for all supports are probably due to the rapid reaction between H<sub>2</sub> and oxygen on the catalyst surface. From a thermodynamic standpoint, the first and largest peak in all cases would be the reduction of adsorbed oxygen while, two other smaller peaks identifiable between 330 and 430 K may be attributed to the reduction of Mo<sup>4+</sup> and Mo<sup>2+</sup> species left over from the previous sulphide nitridation to Mo atoms. The absence of these two smaller peaks in the silica catalyst may be indicative of complete sulphide nitridation in the preceding step. However, the high temperature peaks (473–773 K) arose from the hydrogenation of NH<sub>2</sub> and N species present on surface after nitridation [17]. The area under these peaks reflect the relative concentration of these surface species and suggest that they may be more on the ZrO<sub>2</sub> and TiO<sub>2</sub> catalyst surface consistent with H<sub>2</sub> uptake and dispersion measurements. It, however, appears that the strength of the Mo–NH<sub>2</sub> bonds is roughly the same on the ZrO<sub>2</sub> and TiO<sub>2</sub> supports as evidenced by the high reduction temperature (ca. 600 K) relative to the Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> catalysts which are located at about 550 and 500 K, respectively.

### 3.3. FT-IR analysis

FT-IR spectra of Mo<sub>2</sub>N on different supports are shown on Fig. 6. Silica-supported Mo<sub>2</sub>N shows a strong peak at 1100 cm<sup>-1</sup>, corresponding to the asymmetric stretching (AS) vibrational mode of the Si–O–Si bridge of the siloxane links [18]. Broadband in the region between 3000 and 4000 cm<sup>-1</sup> possibly assigned to the OH stretching mode due to the presence of moisture in catalyst, and same observation was found from all supports [18]. Alumina-supported Mo<sub>2</sub>N has two small peaks at 1450 and 1485 cm<sup>-1</sup> which are due to the deformational mode of NH<sub>4</sub><sup>+</sup> formed by the interaction of ammonia with the Bronsted acid sites similar to the observations of Nagai et al. [17]. Interestingly those same peaks were also shown on the other supports between 1300 and 1500 cm<sup>-1</sup> albeit with reduced magnitude on the titania catalyst. Maity et al. [19,20] identified tetrahedral and octahedral Mo species in the region between 800 and 1200 cm<sup>-1</sup> and thus, the peaks located between 830–930 and 930–990 cm<sup>-1</sup> are assigned to these surface species. The formation of γ-Mo<sub>2</sub>O<sub>x</sub>N<sub>1-x</sub> and γ-Mo<sub>2</sub>N was also observed in the region of 700–1200 cm<sup>-1</sup> by Zhang et al. [15].

### 3.4. NH<sub>3</sub> temperature programmed desorption

Further catalyst characterisation was therefore carried out using NH<sub>3</sub>-temperature programmed desorption to

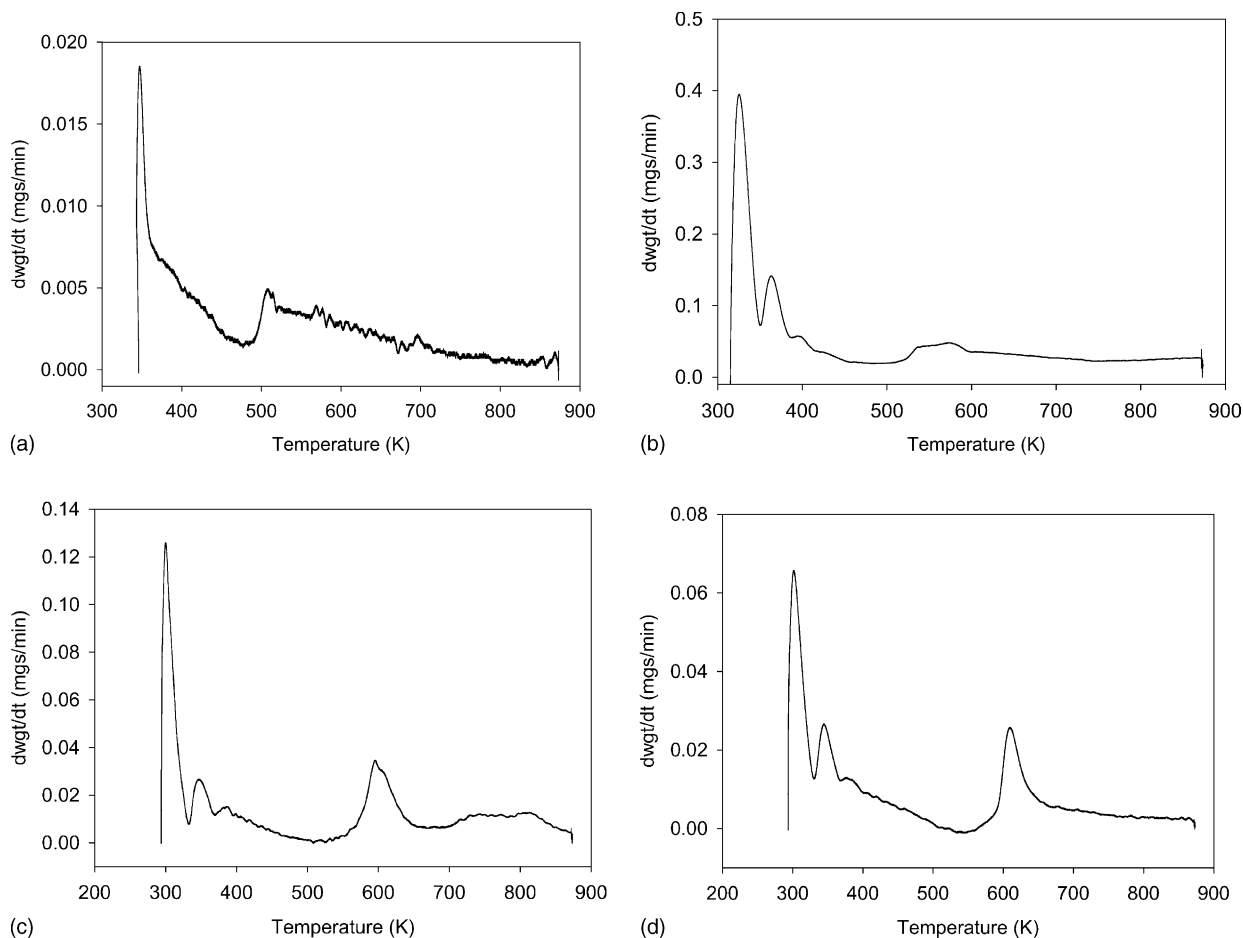


Fig. 5. (a) TPR of 12% Mo<sub>2</sub>N/SiO<sub>2</sub>; (b) TPR of 12% Mo<sub>2</sub>N/Al<sub>2</sub>O<sub>3</sub>; (c) TPR of 12% Mo<sub>2</sub>N/ZrO<sub>2</sub>; (d) TPR of 12% Mo<sub>2</sub>N/TiO<sub>2</sub>.

determine the acid site concentration and strength on all the catalysts. This procedure was performed on the Autochem2910 using 0.4% NH<sub>3</sub>/He at various heating rates (5–15 K min<sup>-1</sup>). Fig. 7 plots the heat of desorption,  $-E_d$ , and relative quantity of NH<sub>3</sub> uptake (A/C) as a function of the support. Interestingly, Mo<sub>2</sub>N/ZrO<sub>2</sub> catalyst which has

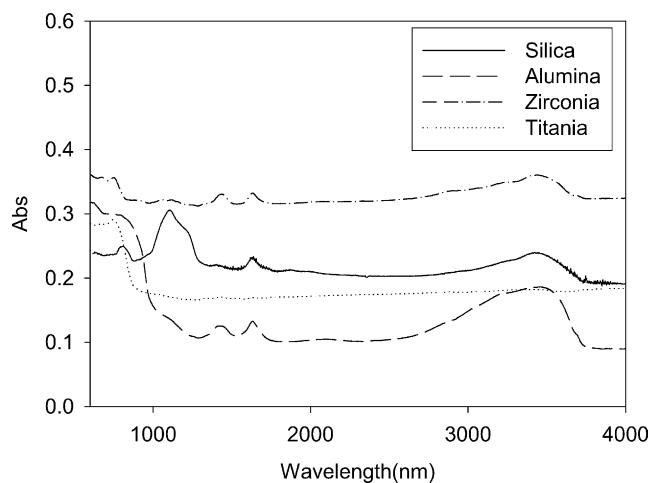


Fig. 6. FT-IR of 12% Mo<sub>2</sub>N on various supports.

highest H<sub>2</sub> adsorption capacity possess the lowest heat of desorption for NH<sub>3</sub> as well as the smallest NH<sub>3</sub> uptake. This would suggest that there is a relatively low concentration of acid sites on this support while the high H<sub>2</sub> capacity was probably due to the presence of high surface Mo atoms since both acid and metal atom sites participate in the H<sub>2</sub> adsorption process. Nevertheless,  $-E_d$  values for SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> are practically the same although the Al<sub>2</sub>O<sub>3</sub>-supported Mo<sub>2</sub>N has the highest NH<sub>3</sub> uptake. It is also apparent that the zirconia acid sites (lowest  $-E_d$ ) are also relatively weak compared to the other three supports.

### 3.5. Fischer Tropsch activity evaluation

All catalysts were evaluated with CO hydrogenation reaction at 553 K and 1 atm in the same reactor where nitridation was performed. Typically, the catalyst was cooled down in the nitriding gas stream to reaction temperature at which point 50% CO/N<sub>2</sub> was mixed with the incoming H<sub>2</sub> before being admitted into the reactor.

Fig. 8 reveals that the Mo<sub>2</sub>N/Al<sub>2</sub>O<sub>3</sub> catalyst is significantly better for hydrocarbon production than all other supports. The trend of the global reaction rate is, similar

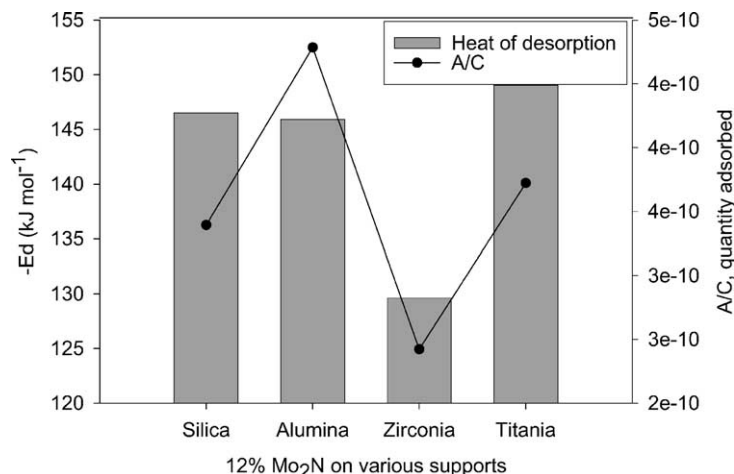
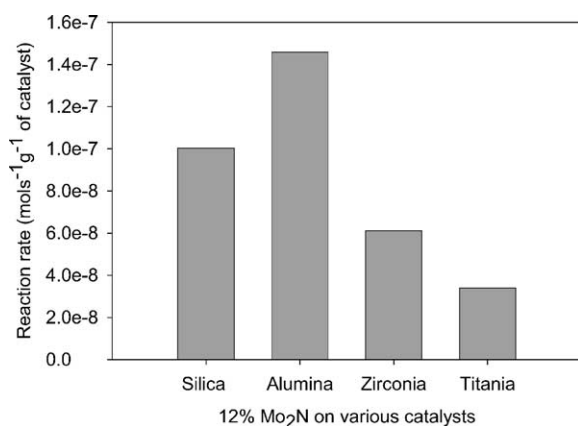
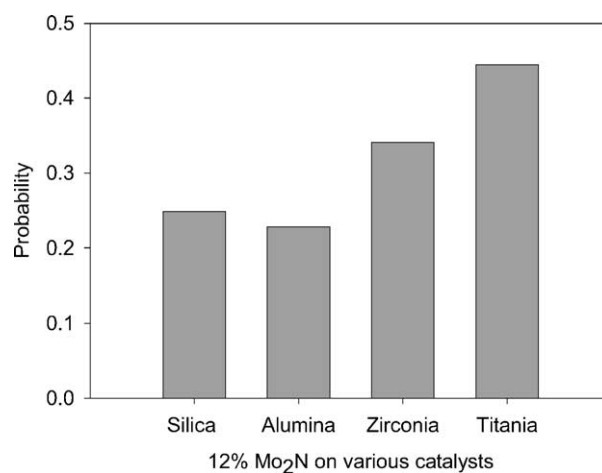
Fig. 7. NH<sub>3</sub> TPD results for all supports.

Fig. 8. Effect of support-type on CO hydrogenation reaction rate.

Fig. 10. Chain growth probability on the Mo<sub>2</sub>N catalysts.

to what has been reported for other noble metal supported on similar oxides [21]. Indeed, comparison on the basis of specific activity or TOF (reaction rate/H<sub>2</sub> uptake) also showed that alumina-supported Mo<sub>2</sub>N (cf. Fig. 9) is still the most superior catalyst for CO hydrogenation. This may

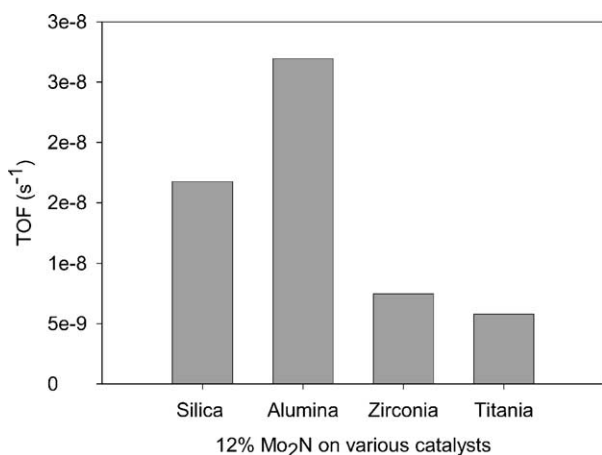


Fig. 9. Turnover frequency of catalysts.

be due to right balance between particle size, acid site density and strength (NH<sub>3</sub> heat of desorption,  $E_d$ ). Interestingly, Pt/alumina has similar characteristics and in fact  $E_d$  for Pt ( $-142 \text{ kJ mol}^{-1}$ ) [22] compares well with Mo<sub>2</sub>N ( $-145.9 \text{ kJ mol}^{-1}$ ) obtained in this study provides further incentive to explore Mo<sub>2</sub>N as a possible cheap replacement for expensive Pt catalyst in appropriate reactions. However, as seen in Fig. 10, the low chain growth factor,  $\alpha$ , obtained from an Anderson–Schulz–Flory plot of the product distribution (C<sub>1</sub>–C<sub>5</sub> hydrocarbons) indicates that there is scope for further developmental work on this new system.

#### 4. Conclusions

This study revealed that high surface area catalysts may be prepared via nitridation of MoS<sub>2</sub> obtained from PFHS method. High temperature and H<sub>2</sub>:NH<sub>3</sub> ratio favoured high area generation suggesting that the MoS<sub>2</sub> was first reduced by H<sub>2</sub> followed by incorporation of N atoms into the



interstitial space between Mo atoms. Comparison between silica, alumina, zirconia and titania as supports showed that alumina catalyst has the highest surface area but H<sub>2</sub> chemisorption was superior on the zirconia and titania supports. However, there was no evidence of H<sub>2</sub> spillover or extra adsorption on interface between Mo<sub>2</sub>N species and the support (support–interaction). The trend in the global hydrocarbon production rate parallels that seen during NH<sub>3</sub>-TPD in terms of acid site population and strength, Mo<sub>2</sub>N/Al<sub>2</sub>O<sub>3</sub> catalyst was the most active catalyst and possess also the highest turnover frequency. Although further developmental work is required to improve the chain growth probability of the alumina catalyst, present data suggest that Mo<sub>2</sub>N has Pt-like behaviour and may be a cheaper option for FT catalysis in the overall quest for economical gas-to-liquid technology.

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