Catalytic hydrodenitrogenation of indole over molybdenum nitride and carbides with different structures

Senzi Li[a], Jae Sung Lee[a,*], Taeghwan Hyeon[1,b], Kenneth S. Suslick[b]

[a]*Department of Chemical Engineering and School of Environmental Engineering, Pohang University of Science and Technology, Pohang, Seoul 790-784, South Korea*
[b]*School of Chemical Science, University of Illinois at Urbana-Champaign Urbana, IL 61801, USA*

Abstract

The hydrodenitrogenation (HDN) of indole has been studied over Mo_2N and Mo_2C with different structures. The difference in activity was modest and the structure of the catalysts exerted a more significant effect than the chemical composition. More evident difference was observed in selectivity, and here the composition was the most important factor. Sonochemically prepared Mo_2C was an active catalyst for HDN reaction. It formed plate-like aggregates of loosely packed Mo_2C (fcc) particles. The crystallinity of sonochemically prepared Mo_2C was improved during the reaction, and its behavior in HDN became similar to Mo_2C (fcc) prepared by the TPR method. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hydrodenitrogenation (HDN), a treatment process to remove organonitrogen compounds from petroleum or coal-derived feedstocks, is one of the hydropurification processes in the oil refinery industry. These hydrotreating processes minimize the formation of air pollutants and poisoning of the catalysts used in the downstream. Group IV and group VIII metal sulfides supported on alumina, typically Co(Ni)–Mo/γ-Al_2O_3, have been used as commercial hydrotreating catalysts for more than 40 years. In recent years, however, these catalysts are facing strong challenges from more stringent environmental constraints and needs of utilizing low quality hydrocarbon feedstocks. Their drawbacks include excessive hydrogen consumption and the requirement of severe operating conditions such as high temperatures and pressures. Thus, environmental problems and energy saving motives have become a driving force for developing new hydrotreating catalysts.

A temperature-programmed reaction method was introduced by Boudart and coworkers [1–4] to synthesize unsupported Mo_2N and Mo_2C powders with high specific surface areas. Since then, a variety of hydrogen transfer reactions including hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) have been studied over supported and unsupported molybdenum nitride and carbide catalysts, and some encouraging

*Corresponding author. Tel.: +82-562-279-2266; fax: +82-562-279-5799; e-mail: jlee@postech.ac.kr
[1]Present address: School of Chemical Engineering, Seoul National University, Seoul 151-742, South Korea.

results have been obtained [5–10]. Lee and Boudart [5] found that unsupported α-MoC$_{1-x}$ has thiophene HDS activity comparable to that of sulfided Mo/Al$_2$O$_3$. Schlatter et al. [6] reported that Mo$_2$N and Mo$_2$C showed quinoline HDN activity comparable to that of commercial sulfided Ni–Mo/Al$_2$O$_3$. Markel and Van Zee [7] revealed a strong resistance property of Mo$_2$N against being sulfided in thiophene HDS. Choi et al. [9] investigated pyridine HDN on molybdenum carbides with different specific surface areas. Most of the above results have shown that molybdenum nitrides and carbides are superior to or comparable to commercial hydrotreating catalysts.

Recently Suslick et al. [11–13] have developed a new synthetic technique, i.e., sonochemical synthesis of nano-structured inorganic materials, to produce molybdenum carbide powders with high specific surface areas. When solutions of volatile organometallic compounds are irradiated with high intensity ultrasound, high surface area solids are produced consisting of agglomerates of nanometer clusters. They have synthesized nano-structured molybdenum carbides from the ultrasonic irradiation of molybdenum hexacarbonyl. The catalytic studies of dehydrogenation of cyclohexane and hydrogenolysis of ethane over the produced materials have shown that sonochemically prepared molybdenum carbide is a highly selective dehydrogenation catalyst [13].

Motivated by our previous work revealing that Mo$_2$N is an active catalyst for HDN of indole [14], we investigated HDN of indole over different phases of Mo$_2$C and Mo$_2$N, aimed at obtaining an insight into the effect of structures of molybdenum carbides and nitride on the reaction rates and selectivity of HDN of indole. Since nano-structured Mo$_2$C has shown its catalytic potential in a variety of reactions, HDN of indole over sonochemically prepared Mo$_2$C was also investigated.

2. Experimental

2.1. TPR synthesis of Mo$_2$N and Mo$_2$C

A temperature-programmed reaction (TPR) procedure was employed for the preparation of molybdenum nitride and carbides with different crystal structures. For each batch, 4 mmol MoO$_3$ was loaded

in a U-shaped quartz reaction cell stuffed with a plug of quartz wool at the bottom to hold the powders. The temperature of the synthesis reactor was controlled by a PID controller with a local thermocouple mounted axially along the length of the reactor which was located in an electric furnace. To produce Mo$_2$N with face-centered cubic structure (hereafter designated as Mo$_2$N (fcc)), a stream of NH$_3$ (Matheson, 99.99%) was passed through the reaction cell at a flow rate of 135 µmol s^{-1}. Following rapid heating to 500 K, the sample was further heated to 973 K with a linear ramping rate of 30 K h^{-1} and then maintained at the final temperature for 1 h. Once the reaction was complete, the gas flow was switched to a flow of helium (25 µmol s^{-1}) prior to quenching the catalysts. Repeating the same TPR procedure over the produced Mo$_2$N (fcc) but changing the gas from NH$_3$ to a gas mixture of CH$_4$ and H$_2$ with mole ratio of 1:4 (CH$_4$/4H$_2$) at the same flow rate, Mo$_2$C with face-centered cubic structure (hereafter designated as Mo$_2$C (fcc)) was then prepared. Mo$_2$C with hexagonal-closed packed structure (hereafter designated as Mo$_2$C (hcp)) was synthesized from MoO$_3$ by introducing a gas mixture of CH$_4$/4H$_2$ directly instead of NH$_3$ at the same flow rate. All the catalysts were prepared at atmospheric pressure.

2.2. Sonochemical synthesis of Mo$_2$C

Nano-structured Mo$_2$C (fcc) was prepared by a sonochemical apparatus using a high-intensity ultrasonic horn connected to a piezoelectric ceramic and a power supply (Sonic and Materials, model VC-600, 0.5 in. Ti horn, 20 kHz, 100 W cm^{-2}). Sonochemical decomposition of molybdenum hexacarbonyl in hexadecane with high-intensity ultrasound under argon at 363 K for 3 h produced a powder. The black powder was filtered, washed several times with purified and degassed pentane, and heated to 373 K under vacuum. All manipulations for the preparation of samples were performed using vacuum lines and an inert atmosphere box (<1 ppm O$_2$). Elemental analysis of the produced material confirmed its stoichiometry of 2 Mo/C. This sonochemically prepared Mo$_2$C (hereafter designated as sono-Mo$_2$C) contained a small amount of oxygen. Since the presence of oxygen could poison the catalyst, it was removed before catalytic reaction by heating the produced carbides at 573 K for 1 h and

then at 773 K for 48 h in an equal molar mixture of CH_4 and H_2 with a total flow rate of 20 $\mu mol\ s^{-1}$.

2.3. Hydrodenitrogenation (HDN) of indole

Indole, a common organonitrogen compound in the crude oil, was chosen as the representative substrate to test HDN reaction. Unless otherwise indicated, HDN reaction was conducted by the following procedure. Typically, 2 mmol catalysts were used for each run. HDN of indole was carried out in situ without exposing the catalysts to air after preparation. The catalysts were pretreated at 673 K for 1 h under a flow of hydrogen (Union Carbide, 99.999%) at a rate of 15 $\mu mol\ s^{-1}$ prior to the delivery of indole. Indole (Aldrich, 99+%) was introduced into a flow of hydrogen (90 $\mu mol\ s^{-1}$) via a syringe pump (Saga Instruments) at a pumping rate of 0.1 $cm^3\ h^{-1}$ at atmospheric pressure. A vaporization chamber filled with glass beads was positioned upstream of the quartz reactor to ensure a complete mixing of gases. The reaction products were monitored by an on-line HP 5890 gas chromatography (GC) equipped with an FID detector and with a mass selective detector (HP 5971 MDS). An STB-1 capillary column (60 m$\times$0.25 mm$\times$0.25 μm) of Supelco was used to separate products for GC/MS analysis.

The hydrodenitrogenation of indole as a function of reaction temperature was performed following a temperature ramping program from 573 to 773 K. The reactor was maintained at the indicated temperature for 2 h prior to moving to the next temperature level at a ramping rate of 0.083 $K\ s^{-1}$. The effluent products were analyzed every 15 min via a six-port sampling valve attached on GC. The average value of the last three samplings was taken as the representative rate at the indicated temperature since slow deactivation occurred with time on stream.

2.4. Characterization of catalysts

Since fresh molybdenum carbide and nitride were air sensitive, the samples were passivated prior to characterization. The passivation causing a mild surface oxidation was done by exposing the reactor cell with both ends of the reactor open to the atmosphere for 10 h before taking the samples out of the reactor cell.

The specific surface area (S_g) of the samples was determined on a constant volume adsorption apparatus (Micrometrics ASAP 2021C) by the N_2 BET method. Powder X-ray diffraction (XRD) measurements were conducted using a Mac Science M18XHF diffractometer with Cu K_α radiation. The morphology of passivated samples was observed by scanning electron microscopy (SEM) on a Jeol JSM-840A. For these analyses, samples were mounted on graphite stubs, and gold was sputtered onto them to ensure an adequate conductivity.

3. Results

3.1. Activity of catalysts for HDN of indole

The catalytic behavior of Mo_2N and Mo_2C prepared from TPR and sonochemical synthesis was examined for HDN of indole. Fig. 1 shows conversions of indole as a function of reaction temperature for Mo_2N and Mo_2C catalysts with different structures. The indole conversion increased with increasing temperatures for all the catalysts. For the same catalyst weight, Mo_2N and Mo_2C with face-centered cubic structure gave higher conversions than Mo_2C (hcp) and sono-chemically prepared Mo_2C. However, at temperatures lower than 673 K, sono-chemically prepared Mo_2C dis-

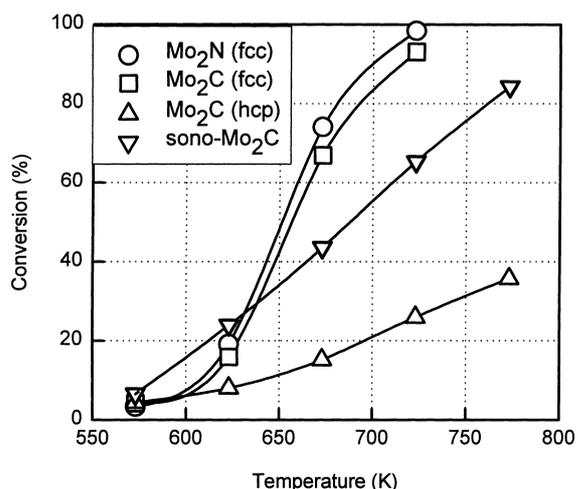Fig. 1. Catalytic activity as a function of temperature over Mo_2N and Mo_2C in indole HDN. Indole feeding rate=0.1 $cm^3\ h^{-1}$, H_2 flow rate=90 $\mu mol\ s^{-1}$, catalyst loading=2 mmol.

Table 1
Specific surface area (m^2 g^{-1}) of Mo$_2$N and Mo$_2$C for HDN of indole

	Mo$_2$N (fcc)	Mo$_2$C (fcc)	Mo$_2$C (hcp)	Sono-Mo$_2$C (fcc)
Before reaction	170.8	163.2	88.3	188
After reaction[a]	84.1	76.8	43.9	91.2

[a] After HDN of indole under the conditions reported in Fig. 1.

played a slightly higher initial activity. In terms of the rates of indole conversion per unit surface area of fresh catalysts (Table 1), Mo$_2$C (hcp) showed the highest HDN rate, followed by sono-Mo$_2$C and then Mo$_2$N (fcc) and Mo$_2$C (fcc). However, these rates per unit surface area were consistent among all catalysts within a factor of 2.5. The greatest difference was observed at 573 K where Mo$_2$C (hcp) was more active than Mo$_2$C (fcc) or Mo$_2$N (fcc) by a factor of 2.5. The rate for sono-Mo$_2$C fell in the middle. If one considers the different structures, compositions and surface areas of these catalysts, the difference in activity among them is remarkably small. Thus it could be concluded that the catalytic activity of molybdenum carbides and nitrides in HDN of indole was not greatly affected by their structure and chemical composition.

3.2. Selectivity of HDN of indole

Fig. 2 gives the product distributions of arylamine and hydrocarbon compounds as a function of temperature for HDN of indole over Mo$_2$N and Mo$_2$C catalysts. Alkanes, benzene, toluene, ethylbenzene, aniline, methylaniline as well as ethylaniline were major products during the HDN reaction. Since the amount of the other aromatic derivatives were less than 2 wt% of the total products, their selectivity values were not presented here. The product distributions showed a strong dependence on reaction temperature for all these catalysts. Roughly, the selectivity to arylamine compounds declined with increasing reaction temperatures whereas that of hydrocarbon compounds increased with increasing reaction temperatures. This indicates that the scission of C–N bonds needs higher activation energy than that of C–C bonds.

In spite of this general trend of selectivity with reaction temperatures, the distribution of products was significantly varied among these nitride and carbide catalysts. Mo$_2$C (fcc), regardless of preparation methods, gave preference to ethylaniline at low temperatures and to saturated hydrocarbons at high temperatures. Around 80% of the products were alkanes when indole was completely converted at 723 K.

For Mo$_2$C (hcp), ethylaniline was the overwhelming product at low temperatures. Since the purpose of HDN is to remove organonitrogen from indole, the higher initial rate of indole conversion over Mo$_2$C (hcp) at low temperatures is not translated into higher HDN activity because major product molecules still contained nitrogen in their structures. On the contrary, Mo$_2$C (hcp) showed considerably lower activity than either Mo$_2$C (fcc) or Mo$_2$N (fcc) at high temperatures when substantial HDN reaction occurred. Different from its Mo$_2$C (fcc) counterparts that gave high preference to alkanes at high temperatures, Mo$_2$C (hcp) showed selectivity advantages for alkylbenzene compounds with toluene being emerged to be the predominant product at temperatures higher than 623 K.

Unlike the product distributions over Mo$_2$C catalysts, Mo$_2$N (fcc) distinguished itself by its high selectivity to benzene and toluene. Aniline and methylaniline rather than ethylaniline were the dominant products at low temperatures, whereas benzene and toluene were the most abundant products at higher temperatures. The selectivity to alkanes was suppressed to a moderate level over the whole temperature range. It is notable that the selectivity to alkanes accounted for less than 30% whereas that to benzene and toluene was near 70% at 723 K, at which point the HDN of indole was complete. The lower selectivity to alkanes for Mo$_2$N (fcc) and Mo$_2$C (hcp) represents less hydrogen consumption, which is of great economic significance in industrial hydrotreating processes.

3.3. Regeneration of sono-Mo$_2$C by H$_2$ treatment

Deactivation of Mo$_2$N (fcc) during HDN of indole was reported elsewhere [14]. The major cause of deactivation was the decrease in the surface area due to the deposition of nitrogen on the catalyst. After the HDN reaction with increasing temperatures, the used sono-Mo$_2$C was treated with H$_2$ at a flow of 135 μmol s^{-1} for 15 h. HDN of indole was then
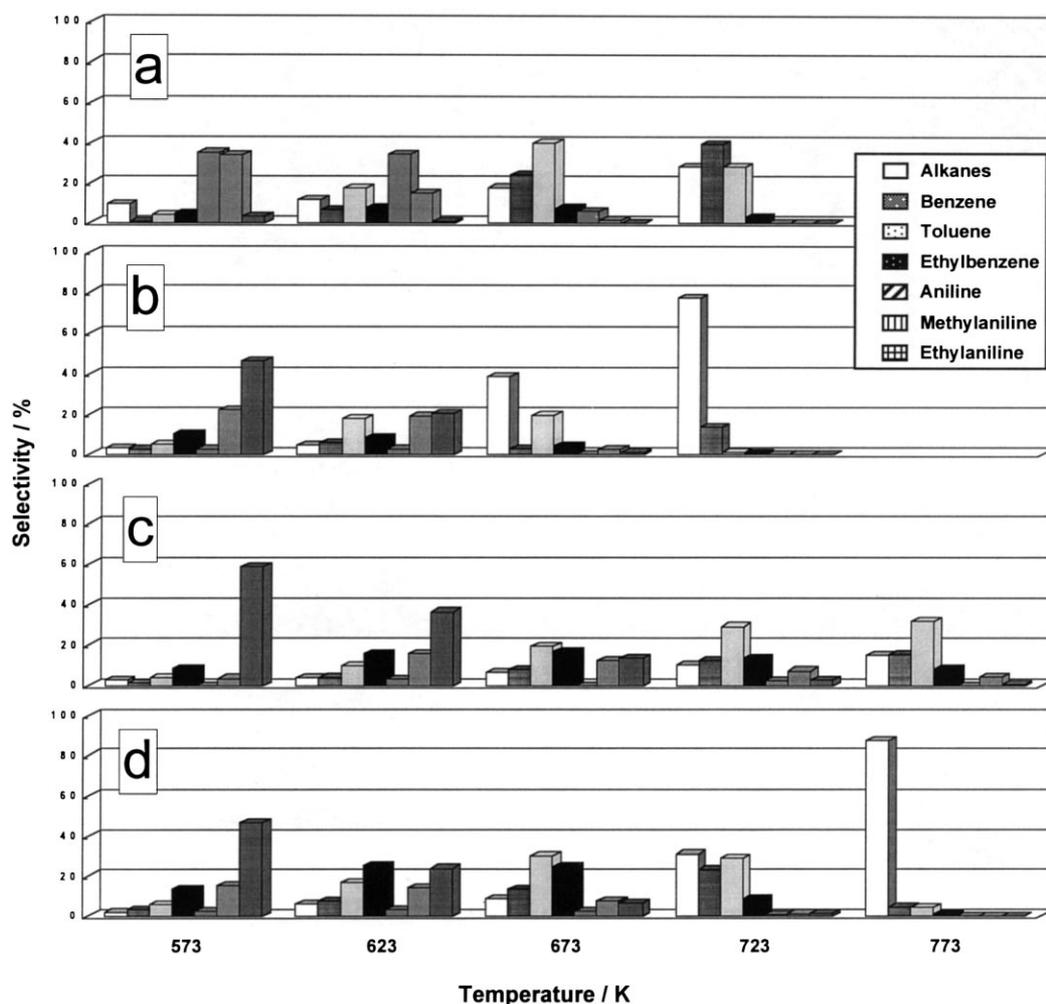
Fig. 2. Product distributions as a function of temperature over Mo_2N and Mo_2C with different structures for HDN of indole: (a) Mo_2N (fcc); (b) Mo_2C (fcc); (c) Mo_2C (hcp) and (d) sono-Mo_2C. Indole feeding rate=0.1 cm^3 h^{-1}, H_2 flow rate=90 μmol s^{-1}, catalyst loading=2 mmol.

carried out isothermally at 673 K for 7 h. The activities were monitored with time on stream and the results are given in Fig. 3. Although the reaction rate decreased by nearly 40% before reaching a steady state after 5 h reaction, the initial reaction rate of indole conversion per unit surface area of the fresh catalyst (8.1 μmol m^{-2} h^{-1}) was comparable to that of fresh catalyst at 673 K (8.9 μmol m^{-2} h^{-1}). This indicates that most of the sites on the catalyst were regenerated after the H_2 treatment. The distribution of reaction products was shown to vary progressively as the reaction proceeded with the concentration of hydrocarbon compounds decreased, while that of

arylamine compounds increased with time on stream. This indicates a selective deactivation of deep hydrogenolysis sites during the initial stage of the reaction.

3.4. Characterization of catalysts

Three catalysts, Mo_2N (fcc), Mo_2C (fcc) and Mo_2C (hcp) have been extensively characterized [2,4,15]. In the present study, the catalysts were removed from the reactor after HDN reaction and analyzed by X-ray diffraction. X-ray diffraction patterns of Mo_2N and Mo_2C prepared by the TPR method after HDN of indole at different temperatures are shown in Fig. 4.
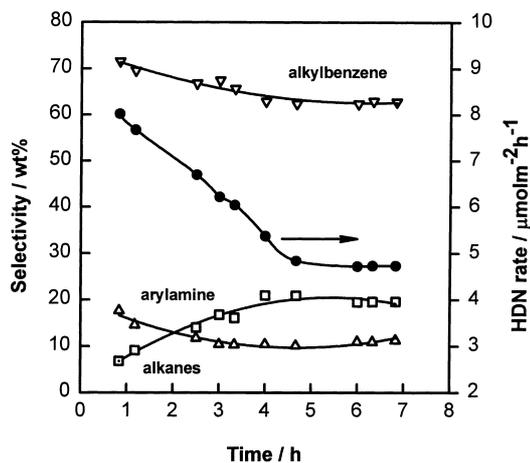
Fig. 3. Variation of reaction rates and selectivity of sonochemically prepared Mo_2C with time on stream for HDN of indole. Indole feeding rate=0.1 cm^3 h^{-1}, H_2 flow rate=90 μmol s^{-1}, catalyst loading=2 mmol, temperature=673 K.

Fig. 4. X-ray diffraction patterns of Mo_2N and Mo_2C after indole HDN at temperatures between 573 and 773 K: (a) Mo_2N (fcc); (b) Mo_2C (fcc) and (c) Mo_2C (hcp).

For Mo_2N (fcc) and Mo_2C (fcc), the higher diffraction intensities of (2 0 0) plane relative to (1 1 1) plane reflect their highly anisotropic nature in morphology
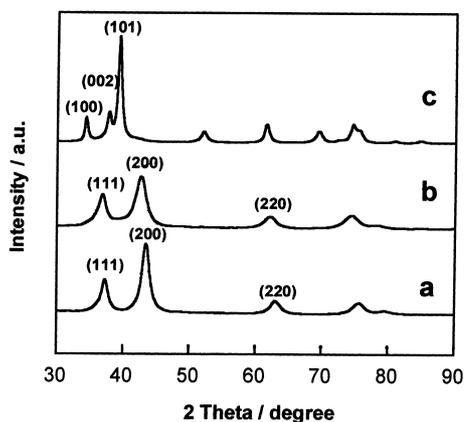
[3], which is generally the consequence of topotactic transformation from anisotropic MoO_3. For Mo_2C (hcp), the relative intensity ratios of diffraction peaks agree well with that of the XRD patterns presented in the standard powder diffraction file [16] with (1 0 1)

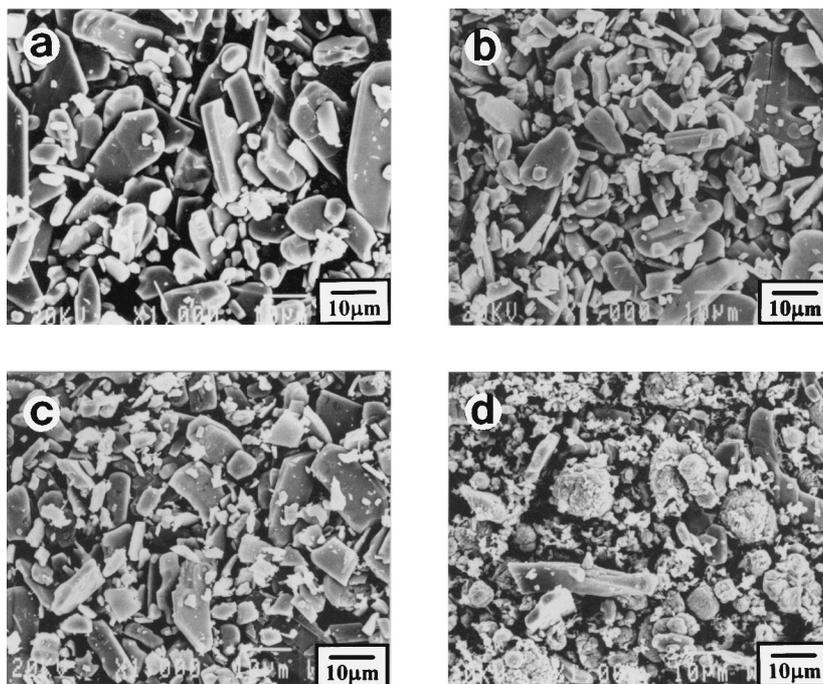Fig. 5. Scanning electron microscopy showing morphologies of (a) MoO_3, (b) Mo_2N (fcc), (c) Mo_2C (fcc) and (d) Mo_2C (hcp) after indole HDN at temperatures between 573 and 773 K. The dark backgrounds represent graphite stubs that were used to support sample powders.

plane showing the highest intensity. This indicates that the crystallites of Mo_2C (hcp) have random morphology without any preferential orientation.

The morphologies of Mo_2N and Mo_2C prepared by the TPR method were observed after HDN reaction and are illustrated in SEM micrographs shown in Fig. 5. The morphologies of all these catalysts regardless of structures were retained after reaction. As expected from the XRD intensity distribution, the morphologies of Mo_2N (fcc) and Mo_2C (fcc) were highly anisotropic and identical to that of their precursor MoO_3 (Fig. 5(a)). In contrast, Mo_2C (hcp) assumed a completely different morphology. This observation reflects the topotactic nature of synthesis process of Mo_2N (fcc) and Mo_2C (fcc), and the non-topotactic route taken by Mo_2C (hcp) [4].

Regarding sonochemically prepared powders, molybdenum metal was expected to be formed. However, X-ray powder diffraction of fresh catalyst showed extremely broad peaks which did not match the pattern of body-centered cubic molybdenum metal. After He treatment at 723 K for 12 h, sharper peaks which matched face-centered cubic molybdenum carbide Mo_2C (fcc) were observed (Fig. 6). Unlike Mo_2N and Mo_2C, prepared from TPR of MoO_3 and consisting of crystallites of anisotropic orientation, sonochemically prepared Mo_2C are comprised of crystallites of isotropic orientation as reflected by its relatively higher intensity of (1 1 1) plane. The diffraction peak of (2 0 0) is so broad and
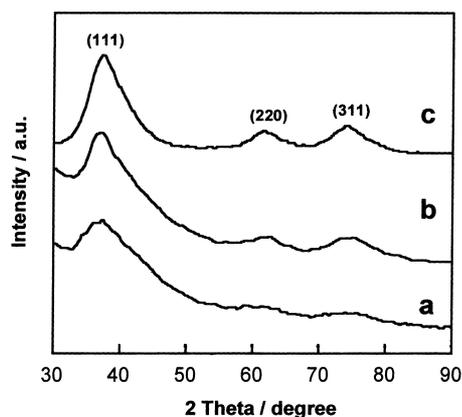
low that it is overshadowed by the broad peak of (1 1 1) reflection.

The surface area of sonochemically prepared Mo_2C after reaction was measured to be 91.2 $m^2\ g^{-1}$. Nearly half of the initial surface area was lost after reaction. The fresh catalyst showed a surface area of 188 $m^2\ g^{-1}$ as reported in Table 1. It is noteworthy that the decreases in surface area by half from the original value for all catalysts were in line with the
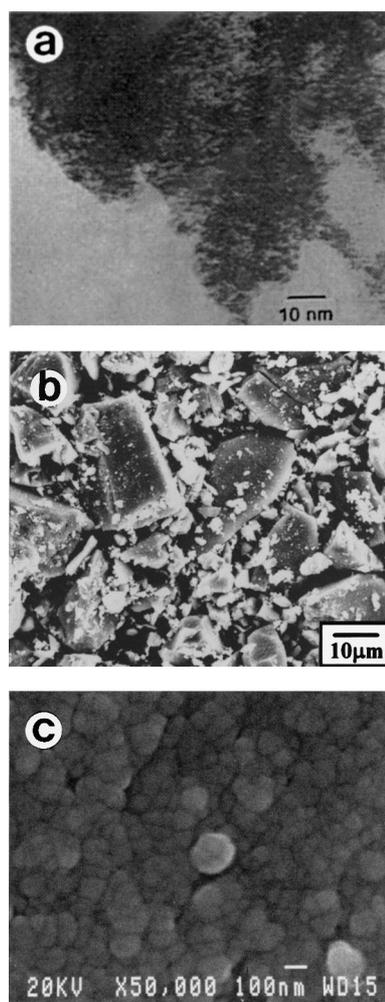
Fig. 7. Transmission electron microscopy showing morphologies of sono-chemically prepared Mo_2C before reaction (a), scanning electron microscopy showing morphology after indole HDN at temperatures between 573 and 773 K, overall morphology (b) and detailed morphology of a platelet (c). The dark backgrounds in (b) and (c) represent graphite stubs that were used to support SEM sample powders.

Fig. 6. X-ray diffraction patterns of sonochemically prepared Mo_2C (a) after synthesis, (b) after He treatment at 723 K for 12 h and (c) after indole HDN at temperatures between 573 and 773 K.

decreases of HDN activity. Except for sono-Mo_2C, where a significant growth of crystallinity was observed after the reaction, there was no evident change in XRD intensity for all the other catalysts after the HDN reaction. Thus, the decrease in the surface area and HDN activity were not due to sintering of the catalyst particles for Mo_2N and Mo_2C prepared from TPR method.

The high resolution TEM in Fig. 7(a) shows that sono-Mo_2C consists of particles of ca. 2 nm. The morphology of sono-Mo_2C (Fig. 7(b)) shows that the nano-sized fine particles agglomerated to form larger aggregates of a platelet shape after HDN reaction. However, the shape of primary particles observed by highly magnified SEM (Fig. 7(c)) was a round isotropic one in agreement with XRD intensity distribution (Fig. 6). This growth of particles might, in part, result in the loss of surface area and probably contributes to the deactivation.

4. Discussion

Catalytic activity and selectivity of a solid could be affected by many factors such as structure, chemical composition and crystallinity. Usually these factors are coupled, and it is difficult to separate their effects. The four catalysts studied here provide an opportunity to discern some of these effects. We have the same structure with different chemical compositions in Mo_2N (fcc) and Mo_2C (fcc), the same chemical composition with different structures in Mo_2C (fcc) and Mo_2C (hcp), and different degrees of crystallinity in Mo_2C (fcc) and sono-Mo_2C. Because all the catalysts are unsupported bulk materials, the intrinsic reaction behavior could be conveniently compared without concern about any support effects.

Irrespective of the differences in structure and preparation method of Mo_2N and Mo_2C, the identical products and the similar evolution of product distributions with reaction temperature and time on stream for HDN of indole suggest that the HDN proceeds through the same reaction pathway over all these catalysts. As proposed in our previous paper [14], the HDN of indole over Mo_2N and Mo_2C catalysts involves saturation of heterocyclic ring to form indoline, followed by partial cleavage of C–N bonds to form *o*-ethylaniline, and then simultaneous hydrogenolysis of C–C and C–N bonds, leading to a variety of arylamine and alkylbenzene compounds. Parts of produced alkylbenzene might go through hydrogenation and hydrogenolysis, yielding alkanes.

Despite the same reaction pathway, there is a modest difference in activity and a marked difference in selectivity of Mo_2N and Mo_2C catalysts. As shown in Fig. 1, four catalysts give different indole conversions. When the surface areas are considered, however, the difference in rates is within a factor of 2.5 in the whole temperature range. This discrepancy is much smaller compared to that for ethane [17] or butane [18] hydrogenolysis that showed at least an order of magnitude difference between Mo_2C (hcp) and Mo_2C (fcc). The hydrogenolysis of alkane is the most typical structure-sensitive reaction [19]. On the other hand, there was essential difference between the two catalysts in selectivity, especially in the hydrogenation activity of alkylbenzene compounds. In any case, the difference in HDN activity and selectivity between these two catalysts of the same stoichiometry may arise from their differences in structure. For Mo_2C (hcp), due to the staggered arrangement of molybdenum and carbon atoms in (1 0 1) plane, not only the molybdenum atoms on the outermost surface but also the atoms closely next to it are likely to be exposed to gas phase reactants. However, for Mo_2C (fcc), the second layer molybdenum atoms on (2 0 0) plane lie directly beneath the carbon atoms, and consequently are inaccessible to reactant. Thus, the surface of Mo_2C (hcp) is more open than that of Mo_2C (fcc). If this difference in site density (exposed Mo atoms per unit surface area) is taken into account, the difference by the factor of 2.5 in the rates of indole conversion between catalysts of hcp and fcc structures almost disappears. The fact that Mo_2N and Mo_2C with fcc structure give similar activity values suggests that the structural effects are more important than the difference in catalyst composition for catalytic HDN activity. In the case of sono-Mo_2C, the diffraction pattern shows much broader peaks with more intense diffraction for (1 1 1) plane than for (2 0 0) plane (Fig. 6). In spite of the fcc structure it possesses, the relative intensity of (1 1 1)/(2 0 0) is different from that of Mo_2C (fcc) of anisotropic nature, suggestive of its randomly distributed crystallites. The discrepancy in morphology and crystallinity might be related to the modest difference in their activity.

The selectivity differences between molybdenum carbides and nitride are more evident than those among molybdenum carbides with different structures (Fig. 2). It should be mentioned that differences in selectivity among catalysts are observed even at low temperatures where difference in indole conversions is small. Thus the observed differences reflect an intrinsic nature of the catalysts and have not originated from different indole conversions. Schlatter et al. [6] carried out the quinoline HDN reaction over Mo_2C and Mo_2N in a batch reaction system at high pressures, and reported that both catalysts were similar in activity, but Mo_2C showed considerably higher selectivity to aromatic products than Mo_2N. However, in our flow reactor system for HDN of indole at atmospheric pressure, Mo_2N (fcc) and Mo_2C (fcc) gave similar activity but Mo_2N showed higher selectivity to hydrogenolysis of saturated C–C bonds with lower selectivity to the ring hydrogenation, resulting in selectivity preference to alkylbenzene compounds. In contrast, Mo_2C (fcc) showed preferential formation of alkanes particularly at higher temperatures. The different behaviors of Mo_2N and Mo_2C in activity and selectivity were also observed by Choi et al. [9] for HDN of pyridine.

Although Mo_2N and Mo_2C do not always show a consistent behavior in different reaction systems, the difference in selectivity in this study seems to originate from the difference of electronegativity between nitrogen and carbon. Since nitrogen is more electronegative than carbon, Mo_2N should possess more Lewis acidity than that of Mo_2C. Thus, basic aniline compounds will adsorb more readily on Mo_2N. As a result, the activation of C–N bond of ethylaniline leads to the facile formation of toluene and benzene and the suppression of the hydrogenation of benzene ring compared to Mo_2C.

Our previous investigation [14] revealed that deposition of nitrogen was the main reason for the deactivation of HDN of indole over Mo_2N. This assumption could be extended to Mo_2C catalysts. Since nitrogen is a little more electronegative than carbon, it is likely that NH_3 or the nitrogen fragments adsorb strongly on the active sites, which accounts for the decline of activity with time on stream and the shift of the main product from hydrocarbons to arylamine compounds. The deactivation was accompanied by progressive loss of surface area, probably due to pore blocking. However, increasing the reaction temperature or treating the catalysts under the flow of hydrogen can remove nitrogen deposits, leaving a clean surface exposed, then the activity can be regenerated as demonstrated here for sono-Mo_2C.

5. Conclusions

Four catalysts have been studied in order to investigate the effects of structure, composition and crystallinity of the catalysts on their activity and selectivity in HDN of indole. The difference in activity was modest and the structure of the catalysts exerted a more significant effect than the chemical composition. More evident difference was observed in selectivity, and here, the composition was the most important factor. Sonochemically prepared Mo_2C was an active catalyst for HDN reaction. It formed plate-like aggregates of loosely packed Mo_2C (fcc) particles. The crystallinity of sonochemically prepared Mo_2C was improved during the reaction, and its behavior in HDN became similar to Mo_2C (fcc) prepared by the TPR method.

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