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Hydrodealkylation of Toluene Using Supported Nickel Catalysts: Effect of Molybdenum on Activity and Selectivity

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Abstract. The effect of the addition of molybdenum to the alumina supported nickel catalysts in the hydrodealkylation of toluene to benzene was investigated. It was observed that the primary effect was the marked reduction in the catalytic activity which was particularly prominent at higher nickel loadings. Practically no eminent change in the selectivity toward the hydrodealkylation reaction or toward the simultaneously occurring hydrogenation and hydrocracking reactions was shown by the incorporation of molybdenum. However, the latter two reactions were found to be influenced by the reaction temperature. The Ni-Mo/Al_2O_3 series of catalysts showed reaction maxima at a specific atomic ratio of nickel and molybdenum suggesting a possible optimized bifunctional mechanism involving the two metal centers. Catalytic activity of the Ni/Al_2O_3 catalysts in particular was clearly influenced by the nickel content and the reaction temperature while a moderate effect was observed for the Ni-Mo/Al_2O_3 catalysts.

Introduction

In addition to a wide application in a number of industrial processes, alumina supported nickel catalyst has also been reported to catalyze the hydrodealkylation of alkylaromatics particularly toluene to form benzene [1]. However, this important reaction process is often complicated by unwanted side-reactions such as hydrogenation [2], ring opening [3], disproportionation and hydrocraking [1] or by an activity loss when used continuously on stream [4] or during regeneration steps. In this connection, the possibility of the properties of nickel being improved when used in conjuction with another metal to form a selective intermetallic catalyst of high activity may be a valuable subject of study. The synergistic effect of multicomponent or multiphase catalysts may well be an alternative route to developing highly specific and stable catalysts.

In a related reaction, the unstable activity of the Ni/Al_2O_3 catalyst for the hydrogenation of benzene has been associated with the sensitivity of the conventional catalyst to sulfur poisoning. Doping the nickel catalysts with molybdenum was shown to result in a catalyst less sensitive to sulfur [5]. Similarly, nickel has been used as a promoter in the preparation of molybdenum catalyst with some notable enhancement on the catalytic performance towards hydrodenitrogenation reaction [6]. These past observations point to the fact that the addition of molybdenum or the use of Ni-Mo bimetallic by some means favors the formation of a catalyst system with enhanced or synergistic characteristics and thus may warrant the investigation of its application towards the hydrodealkylation of toluene.

This study aims to determine the effect of molybdenum on the catalytic properties of the conventional nickel-alumina catalysts in the hydrodealkylation of toluene to benzene. The effect of the nickel loading and the influence of reaction temperature on the activity of the catalysts were also investigated.

Materials and Method

Chemicals

Toluene of more than 99% purity was obtained from Merck, Germany. Further gas chromatographic tests indicated no detectable contaminants. Hydrogen and nitrogen gases were of purity greater than 99.5% and were obtained from the Saudi Industrial Gas Company. These gases were allowed to pass through molecular sieve driers prior to being used in the system.

Catalyst preparation and characterization

Two series of catalysts were prepared by the impregnation method. For the first set, known weights of reagent grade hydrous nickel nitrate, $Ni(NO_3)_2.6H_2O$, were dissolved in tridistilled water and allowed to cover a known amount of 800-100 mesh γ-alumina oxide in a rotary evaporator to correspond to 2, 4, 6 and 8% Ni over Al_2O_3. For the second set of catalysts, a constant weight of reagent grade ammonium molybdate, $(NH_4)_2MoO_4$, was dissolved in water and added to the various weights of nickel nitrate as in the first series to constitute the 2%Ni-12%Mo, 4%Ni-12%Mo, 6%Ni-12%Mo and 8%Ni-12%Mo over Al_2O_3. The mixtures were heated to about 343 K under reduced pressure until a flowing powder is obtained and further oven-dried at 393 K overnight. The Ni/Mo atomic ratio for the second series of catalysts ranged from 0.27-1.09. Reduction was carried out initially by gradual heating to 623 K under a stream of hydrogen (40 ml/min) and continued for 24 hrs. After such time, the temperature was then allowed to decrease slowly to room temperature.

The specific surface area, S_{BET}, as well as the pore volume, V_p, were calculated from the nitrogen adsorption-desorption isotherm at 78 K. The free metal surface area, S_{Ni}, was determined by the hydrogen chemisorption at 298 K.

Hydrodealkylation procedure

Toluene hydrodealkylation (THD) was observed at the temperature range of 550-650 K using the pulse technique and utilizing a continuous flow reactor system as illustrated in Fig. 1. After the weighed amount of catalyst had reached the desired reaction conditions, toluene pulses were introduced to the hydrogen stream allowing pre-

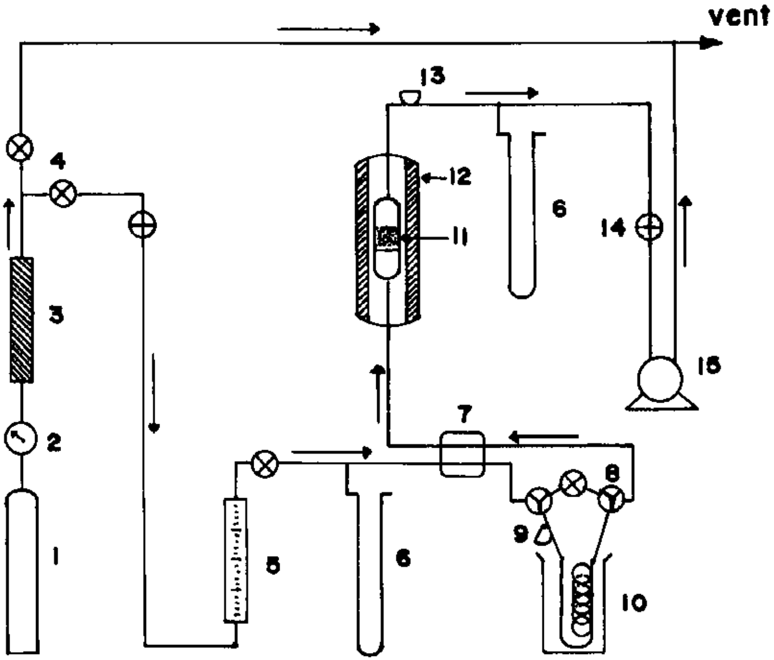

Fig. 1. Schematic diagram of the catalytic flow reactor system.

1. H_2 tank
2. pressure regulator
3. silica gel cartridge
4. shut-off valve
5. rotameter
6. Hg manometer
7. TCD, thermal conductivity detector
8. three-way stopcock
9. reactant injection port
10. constant temperature bath
11. reactor/catalyst bed
12. reactor furnace
13. product sampling point
14. fine metering valve
15. vacuum pump

mixing in a temperature conditioning zone prior to entry to the reactor. All measurements were performed after temperature and flow steady state conditions had been attained as monitored by a thermal conductivity detector (TCD) connected to the system. Conditions were chosen so as to ensure conversion values of less than 10%, thus limiting the reactor response to a differential conversion mode. Rate of THD was calculated based on the following equation;

$$r = \alpha \; F / w$$

where r is the rate in μmol.min^{-1}·g^{-1}, F is the toluene flow rate in μmol.min^{-1}, α is the fraction of toluene converted to products and w is the weight of Ni in g.

Effluents were collected at the campling point after the reactor. Gas chromatographic analysis was made on 20% DC-200 supported on 60/80 mesh chromosorb P column using a flame ionization detector (FID).

Selectivities for hydrodealkylation, S_B, for hydrocracking, $S_C$and hydrogenation, S_H, have been calculated according to the following relation.

$$S_B \;\% = (R_B \times 100) \;/\; (R_B + R_C + R_H)$$

where R_B, R_C and R_H are initial rates of hydrodealkylation, hydrocracking and hydrogenation respectively. S_C and S_H can be calculated in the same way.

It should be noted that the rate of hydrocracking R_C has been calculated as

$$R_C = \left[(\alpha_H - \alpha_B)\right] / 7) \times (F / w)$$

where $\alpha_H$and α_B are mole fractions of methane and benzene, respectively.

Results and Discussion

Data for some of the physical properties of the different catalysts used are given in Table 1. The specific surface area, S_{BET}, as well as the pore volume, V_p, appeared to decrease slightly with increasing nickel content in both series of catalysts. This observation is consistent with the results of Dixon and Sing [7] while studying coprecipitated nickel alumina from 5.4 to 75% loading. No significant difference can be distinguished between the surface areas of Ni/Al_2O_3 and the Ni-Mo/Al_2O_3 catalysts, although a slight decrease in the pore volumes is shown by the latter.

Table 1. Partial characterization data of the different catalysts

Catalysts	S_{BET} ($m^2.g^{-1}$)	V_p ($ml.g^{-1}$)	S_{Ni} ($m^2.g^{-1}$)
2%Ni/Al_2O_3	106.92	0.32	0.28
4%Ni/Al_2O_3	101.18	0.28	0.62
6%Ni/Al_2O_3	102.95	0.28	1.03
8%Ni/Al_2O_3	99.88	0.29	2.48
2%Ni-12%Mo/Al_2O_3	104.96	0.25	0.17
4%Ni-12%Mo/Al_2O_3	97.32	0.22	0.15
6%Ni-12%Mo/Al_2O_3	100.87	0.24	0.26
8%Ni-12%Mo/Al_2O_3	89.47	0.22	0.31

More notable observations were obtained when the catalysts were subjected to hydrogen chemisorption. Although almost insignificant trend is displayed in the various

Ni-Mo/Al_2O_3 catalysts, the metallic nickel surface areas, S_{Ni}, demonstrated a clear dependence on the nickel content particularly with the Ni/Al_2O_3 catalysts (Fig. 2). This is an important indication of the greater availability of the metal active sites for the reaction at higher nickel loading.

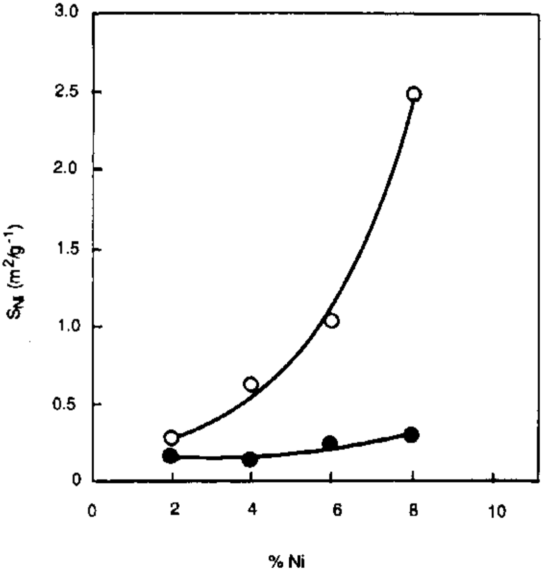

Fig. 2. Nickel surface area as a function of the nickel content (○Ni/Al_2O_3 ; ● Ni-Mo/Al_2O_3).

However, a substantial decrease is generally observed in the metal surface area of the Ni-Mo/alumina catalysts when compared with the catalysts containing Ni/alumina alone, demonstrating a difference by as much as a factor of eight for the highest metal loading. At this point it is worth noting that this observation certainly suggests an important effect of molybdenum which results in some losses of the metal surface area of the Ni catalysts.As will be discussed later, the formation of Ni-Mo interaction products results in the lesser availability or accessibility of the nickel metal for chemical adsorption.

The catalytic activity of the different catalysts

The catalytic activity of both series of catalysts was observed at four different temperatures and is shown as a function of nickel content in Fig. 3. Under the given experimental conditions, the Ni/Al_2O_3 catalysts showed a marked increase in activity

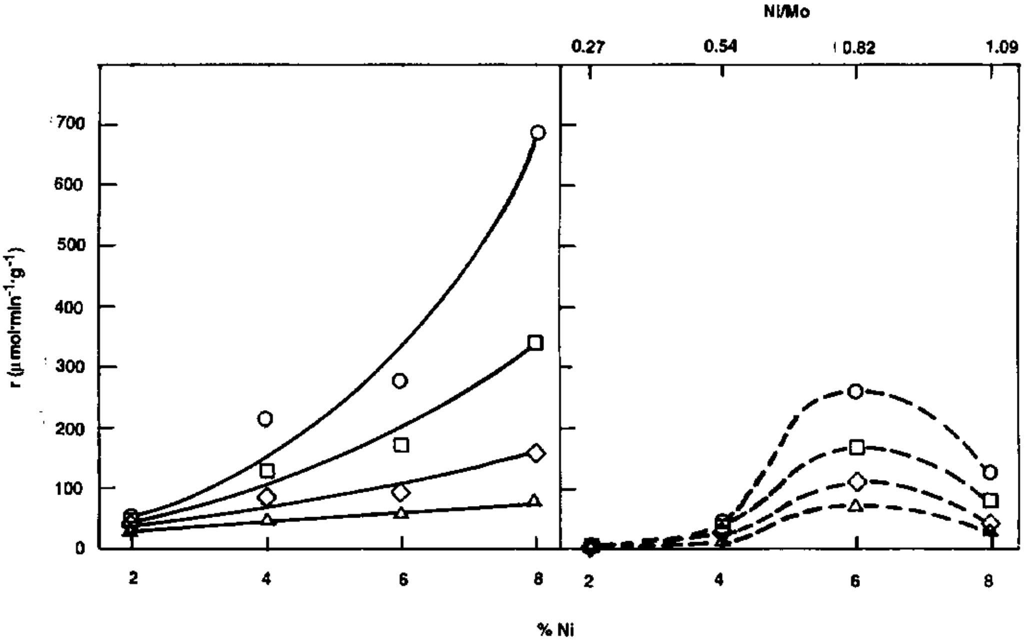

Fig. 3. Reaction rates of the different catalysts as a function of the nickel content or the Ni-Mo atomic ratio obtained at various temperatures (○ 625 K, □ 606 K, ◇ 588 K, △ 571 K).

with increasing Ni content, notably above the 2% nickel loading. It would appear that the high reactivity of alumina towards nickel [8] resulting to what is often referred to as strong metal-support interaction (SMSI) accounts for the prominently low activity at low nickel loading [9-11]. The interaction products at this level of the metal consist mainly of Ni-Al alloys in the form of nickel aluminate spinels [8]. The high degree of difficulty these compounds experience to undergo reduction, of ten times requiring fairly high temperatures, explains the minimal activity observed.

At high nickel content, the nickel catalyst can be described to demonstrate a bimodal nature of "fixed" oxidic nickel species consisting of an amorphous overlayer of nickel oxide interacting but not chemically bound with the support and the spinels of nickel-alumina oxides [12]. The former was found readily susceptible to reduction and thus accounts for the higher metal surface area and the subsequently greater activity observed for the catalysts at higher nickel loading.

However, the activity as a function of the Ni loading for the Ni-Mo/Al_2O_3 series of catalysts showed less significant correlation when compared with the corresponding Ni/Al_2O_3 catalysts. Likewise, the range of catalytic activity of the Ni-Mo catalysts was attained at a much lower rate level. This low activity towards the THD reaction (Fig. 3) may be deduced from the very low metallic surface area of the Ni-Mo catalysts as indicated in Fig. 2. Shielding or dilution effects resulting from the interactions between the active nickel and molybdenum components and/or their interactins with the support at the calcination and reduction stages of catalyst preparation may account for the reduced surface area of the metal.

Similar observation [5] showed reduced toluene hydrogenolysis activity exhibited by the reduciton product of ammonium triammine tetranickel pentamolybdate where the presence of an active Ni-Mo alloy Ni_4Mo was confirmed by magnetic analysis and was therefore suggested to be responsible for the lowering of catalytic activity. Furthermore, the Ni-Mo alloys as well as the excess superficial molybdenum atoms formed upon reduction of $NiMoO_4$ lead to the appreciable decline in the toluene hydrogenolysis reaction and almost complete suppression of the hydrogenation reaction [13]. It may be worthwhile noting that no catalytic activity was demonstrated by Mo/Al_2O_3 alone. This confirmed the essential participation of either the nickel metal or the Ni-Mo ensemble as a requisite for the catalytic activity towards the THD reaction.

An interesting observation is the rate maxima obtained at Ni-Mo ratio of 0.82:1 corresponding to 6% Ni-Mo/Al_2O_3. This clearly points to a significant effect of the molybdenum, which is based on the interaction of the two oxides and possibly suggesting an important bifunctional mechanism for the THD reaction at this particular Ni-Mo atomic ratio. Below or above this ratio, a more limited reaction with the absence of the enhanced effect may be predicted, which indeed showed lower activity. Whereas further study may be necessary to completely elucidate this observation, it would appear that such optimum ratio is not limited to hydrodealkylation alone. For instance, in the case of the hydrodesulfurization reaction [14], the optimum Ni/Mo ratio was found in the order of 0.43, while in the case of hydrocracking of n-heptane [15], the maximum occurred at a

Ni/Mo ratio of about 0.8-1.0. Kozlov and Coworkers [3] studied the activity of two Ni-Mo/Al_2O_3 complexes for the THD reaction using two different atomic ratios: 0.2 and 0.5. Greater activity was demonstrated by the catalyst with 0.5 Ni/Mo ratio.

Thus, it becomes more evident that molybdenum influences the THD reaction in the form of interaction compounds with nickel and that at a particular atomic proportion with the metal (0.82 Ni-Mo ratio) an optimized bifunctional mechanism, resulting to prominently higher catalytic activity compared to the other Ni-Mo catalysts, is at play on the metallic centers [15].

Effect of temperature on catalytic activity

The effect of reaction temperature on the rate of toluene hydrodealkylation using the different catalysts was observed at a constant hydrogen and toluene partial pressures of 710 and 20 Torr, respectively. The reaction rates obtained at different temperatures (571, 588, 606 and 625 K) within the acceptable selectivity range are presented in Fig. 3 and are given as a function of the nickel content of the different catalysts. It can be observed that higher reaction temperature generally resulted in greater activity with a more pronounced influence on the higher loadings of nickel. Almost indistinguishable rate values can be discerned at 2% Ni loadings at the different temperatures used particularly so with the Ni-Mo/Al_2O_3 catalysts. On the other hand, at the maximum loading of 8% Ni for the Ni/Al_2O_3 catalyst, the optimum effect of temperature was exhibited by the increase of the rate from 340 to 689 $\mu mol.min^{-1}.g^{-1}$ at 606 and 625 K, respectively. Moreover, the temperature apparently show less appreciable effect on the activity of the various Ni-Mo/Al_2O_3 catalysts as compared to the corresponding Ni/Al_2O_3 catalysts. Somehow, the Ni-Mo interaction compounds exhibit, to a certain extent, a greater degree of stability with temperature in relation to the nickel/alumina catalysts.

The generated data were used to calculate the apparent activation energy (Ea) and preexponential factor (A) values and are presented in Table 2. Ea was found to vary from 42.0 to 121.9 $kJ.mol^{-1}$ for Ni/Al_2O_3 catalysts and from 30.3 to 88.7 $kJ.mol^{-1}$ for the Ni-Mo/Al_2O_3 catalysts. The trend was for Ea to increase the greater the Ni content.

Table 2. Apparent activation energy and preexponential factor of THD reaction over Ni/Al_2O_3 and Ni-Mo/Al_2O_3 catalysts

Catalyst	Ea ($kJ.mol^{-1}$)	A ($\mu mol.min^{-1}.g^{-1}$)
2%Ni/Al_2O_3	42 ± 4	2.0×10^5
4%Ni/Al_2O_3	85 ± 5	2.8×10^9
6%Ni/Al_2O_3	89 ± 2	8.7×10^9
8%Ni/Al_2O_3	122 ± 1	1.1×10^{13}
2%Ni-12%Mo/Al_2O_3	30 ± 4	2.1×10^3
4%Ni-12%Mo/Al_2O_3	66 ± 6	1.6×10^7
6%Ni-12%Mo/Al_2O_3	71 ± 1	2.4×10^8
8%Ni-12%Mo/Al_2O_3	89 ± 2	3.3×10^9

Likewise, the corresponding A increased from 2.0×10^5 to 1.1×10^{13} μmol.min^{-1}.g^{-1} for the first series and from 2.1×10^3 to 3.3×10^9 μmol.min^{-1}.g^{-1} for the second series of catalysts. The relatively wide variation in Ea values with the proportional increase of the corresponding A at different nickel content suggests a possible role of compensation effect in the reaction. A plot of ln A against Ea has been drawn in Fig. 4.

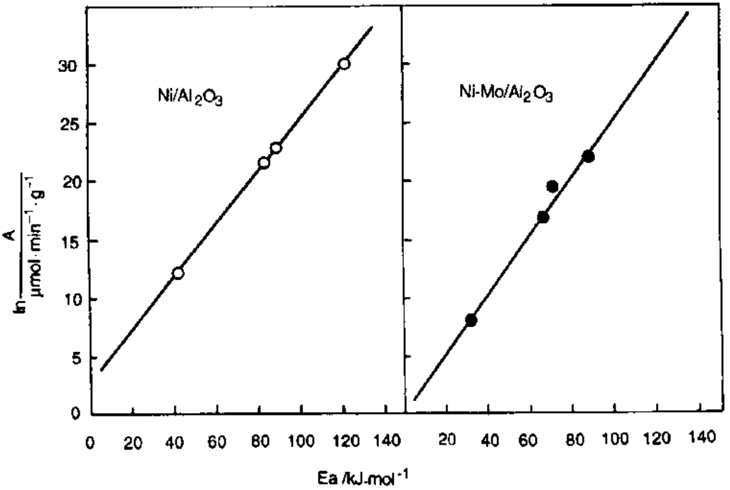

Fig. 4. Plot of activation energy (Ea) against ln A.

Except for the value at 6% Ni-Mo/Al_2O_3, linear relationships between these two parameters were revealed by the two sets of catalysts. Further illustration by the Arrhenius diagram in Fig. 5, indicating intersections for the lines of Ni/Al_2O_3 and Ni-Mo/Al_2O_3, respectively, corroborated the initial observation of the probable role of compensation effect covering not all of the catalysts studied but limited within each series of catalysts.

It is important to note that the isokinetic temperatures (θ_1 = 538 K, θ_2 = 490 K) lie far below the range of temperatures covered by the measurements, giving definite meaning to the linear relationship between ln A and Ea [16, pp. 179-182], and thus providing stronger support for the possible occurrence of compensaiton effect. These observed facts may be best explained in terms of the variations in the densities of active sites from catalysts to catalysts of the same family [17].

The 6% Ni-Mo/Al_2O_3 catalyst corresponding to 0.82 Ni-Mo atomic ratio did not follow the linear trend (Fig. 4) nor shared in the common intersection in the Arrhenius

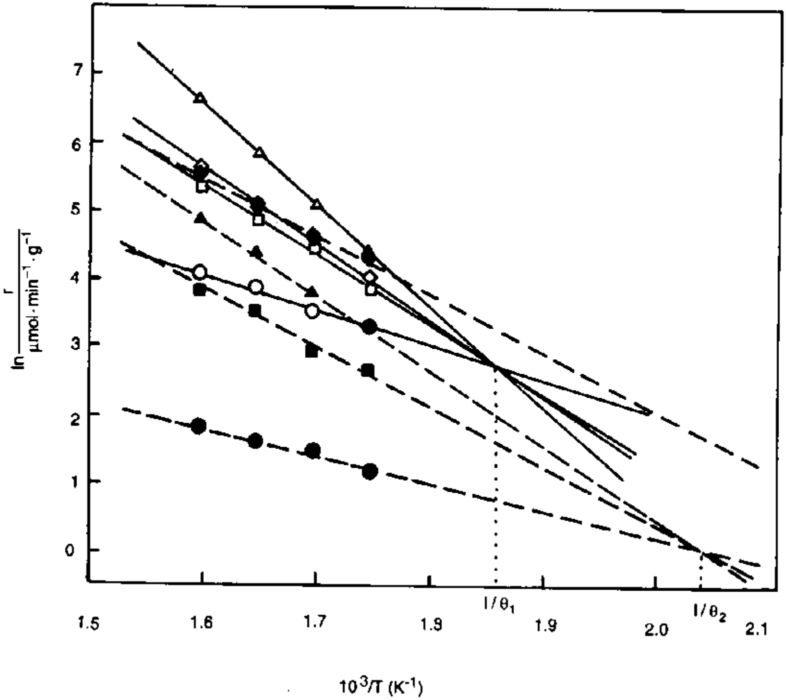

Fig. 5. Plot of the reciprocal of temperature against ln r (Ni/Al_2O_3: O 2% ,□ 4%, ◊ 6%, Δ 8%; Ni-Mo/Al_2O_3:● 2%,■ 4%, ♦ 6%, ▲ 8%).

plot (Fig. 5). This deviation in the catalyst response provides a likely support for a dual function mechanism probably quite distinct from the mechanism followed by the other catalysts in this series and at the same time confirms the observed maxima in the rate curves in Fig. 3.

Effect of temperature on selectivity

The detection of methylcyclohexane, methane and benzene as the only reaction products suggests that under the given reaction conditions the THD reaction proceeds as a result of two competitive reaction processes namely hydrodealkylation and hydrogenation. The former is responsible for the formation of benzene and methane (equation 1) while the latter provides the methylcyclohexane resulting from the exhaustive hydrogenation of toluene (equation 2).

Hydrodealkylation

$$C_6H_5-CH_3 + H_2 \rightarrow C_6H_6 + CH_4 \quad (1)$$

Hydrogenation

$$C_6H_5-CH_3 + 3H_2 \rightarrow C_6H_{11}-CH_3 \quad (2)$$

Kinetic studies conducted by Grenoble [13] show that the THD reaction follow a sequential hydrogenolysis and hydrogenation reaction to form the benzene and methane in stoichiometric proportion. In the present investigation, the detection of the stoichiometrically excess methane suggests subsequent ring opening and hydrocracking of some of the methylcyclohexane (equation 3) after the initial hydrogenation process. Once the ring is opened, all the C-C bonds are promptly cracked to methane as virtually no detectable C_2 to C_6 molecules were observed in the product.

Hydrocracking

$$C_6H_{11}-CH_3 + 7H_2 \longrightarrow 7CH_4 \quad (3)$$

Figures 6 and 7 indicate the general selectivity trends for the Ni/Al_2O_3 and Ni-

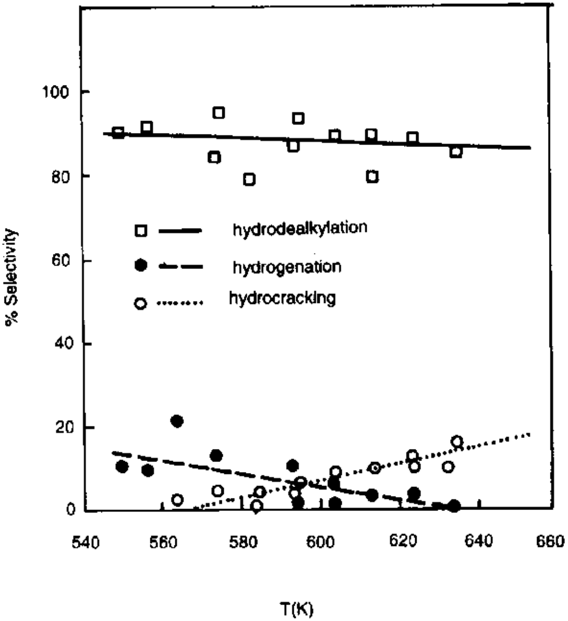

Fig. 6. Selectivity of the reaciton of Ni/Al_2O_3 catalysts at different temperatures.

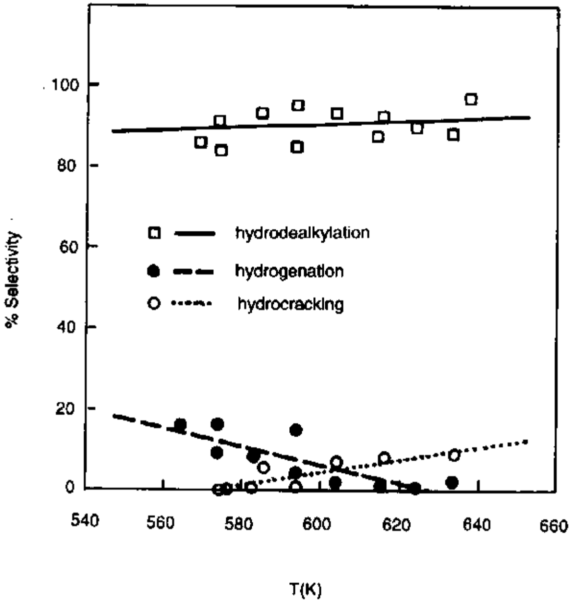

Fig. 7. Selectivity of the reaction of Ni-Mo/Al_2O_3 catalysts at different temperatures.

Mo/Al_2O_3 catalysts, respectively. In both series of catalysts and at the given temperature range 550-650K, the selectivity of both the hydrogenation and the hydrocracking reactions was within the 0-20% level while the selectivity towards hydrodealkylation (formation of benzene) was maintained at 85-90% level. It appears that the addition of molybdenum does not in any practical way influence the selectivity of the alumina catalyst towards the THD reaction.

On the other hand, reaction temperature seems to play a vital role in the selectivity. Although no apparent effect on the formation of benzene can be observed, Figs 6 and 7 clearly indicate the hydrogenation and the hydrocracking reactions counterbalancing each other depending on the reaction temperature. Hydrogenation was predominant at low temperature and as the temperature approaches 570K hydrocracking of the methylcyclohexane commences. Beyond 630K, none of this compound was detected and hydrocracking became the prevailing reaction process.

In a study by Astier *et al.* [5], it has been reported that the selectivity of benzene for the Ni/Al_2O_3 was 83% while for a series of unsupported Ni-Mo catalysts (Ni/Mo ratio ranging from 0.5, 1, and 2) selectivity varied from 66-70%. While our result for both series of catalysts (85-90% selectivity towards benzene) was almost consistent with that of the supported Ni catalysts, the lesser value reported for the unsupported nickel-molybdenum catalysts can be taken to demonstrate a significant role of the alumina support used. It thus appears that the addition of the molybdenum component will not alter the selectivity of the THD reaction as shown by our results as long as the Ni-Mo intermetallic are supported on alumina.

Conclusion

This work has shown that the catalytic properties of the nickel/alumina catalysts toward hydrodealkylation of toluene to benzene was altered by incorporation of molybdenum into the catalyst system. In particular, the resulting alumina supported nickel-molybdenum catalysts generally exhibited a marked reduction in catalytic activity when compared with the supported nickel catalysts alone. This decrease in activity, accompanied by a corresponding reduction in the metal surface area, is brought about by the formation of Ni-Mo interaction products which are finding great difficulty in undergoing a reduction (activation) process.

On the other hand, selectivity to benzene production was maintained at the 85-90% level and was not affected by the addition of the molybdenum. It is most likely that the alumina support plays an important role in maintaining the high selectivity observed.

The catalytic activity of the Ni/Al_2O_3 catalysts was found to be greatly influenced by the nickel content and the reaction temperature far greater than the supported bimetallic catalysts. Of great interest, however, was the rate maximum exhibited by the Ni-Mo/Al_2O_3 catalysts at 0.82 Ni-Mo atomic ratio which probably suggests an important bifunctional mechanism involving the two metallic centers. This observation proved to be very interesting and further investigation along this line will be pursued in our future studies.

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نزع مجموعة الألكيل من التلوين في وجود الهيدروجين باستخدام حفّازات مدعمة من النيكل: تأثير المليبدنوم على الفعالية والانتقائية

سليمان بن حماد الخويطر

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ص.ب ٦٠٨٦، الرياض ١١٤٤٢، المملكة العربية السعودية

(سُلّم في ٢٩ من ذي الحجة ١٤١٥هـ؛ وقُبل للنشر في ١٨ جمادى الآخرة ١٤١٦هـ)

ملخص البحث. أوضحت هذه الدراسة من خلال نزع مجموعة الألكيل من التلوين في وجود الهيدروجين لإنتاج البنزين أنّ الخواص الحفزية لحفّازات النيكل المحمولة على أكسيد الألمنيوم تتغير عندما يدخل المليبدنوم في تركيب الحفّازات. حيث لوحظ أن الفعالية الحفزية تنخفض بشكل واضح في حالة الحفّازات التي يدخل المليبدنوم في تركيبها إذا ما قورنت بفعالية حفّازات النيكل لوحدها. ولقد كان ذلك الانخفاض مصحوبًا بانخفاض في المساحة المعدنية للحفّازات وذلك راجع إلى احتمال تكون نواتج جديدة من تداخل النيكل مع المليبدنوم يصعب تنشيطها خلال عملية الاختزال. ومن ناحية أخرى وجد أن انتقائية إنتاج البنزين من التلوين تتراوح بين ٨٥٪ إلى ٩٠٪ عند استخدام حفّازات النيكل ولم تتأثر هذه النسبة بإدخال المليبدنوم في تركيبها، وقد يكون ذلك راجعًا إلى أن الدعامة (أكسيد الألمنيوم) تقوم بدور مهم للحفاظ على بقاء الانتقائية العالية عند هذا المستوى في كلتا الحالتين، بالإضافة إلى ذلك لم يلاحظ تغير كبير في انتقائية تفاعلي الهدرجة والتكسير المهدرج المصاحبتين لإنتاج البنزين على الرغم من أنهما يتأثران كثيرًا بدرجة حرارة التفاعل. أما بالنسبة لفعاليات حفازات النيكل لوحدها وجد أنها تتأثر كثيرًا بكمية النيكل ودرجة حرارة التفاعل إذا ما قورنت بفعاليات الحفازات التي يدخل في تركيبها المليبدنوم حيث كان تأثرها قليلاً. كما وجد أن فعالية حفازات النيكل والمليبدنوم تصل إلى نهاية عظمى عند نسبة معيّنة (٠,٨٢) من المعدنين وهذا يمكن أن يكون دليلاً على وجود ميكانيكية مزدوجة تشترك فيها المراكز النشطة فيها.