

Kinetic Investigation of the Effect of Nickel and Fluorine on the HDN of Methylcyclohexylamine over WS₂/Al₂O₃ Catalysts

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The effects of incorporation of nickel and fluorine in WS₂/Al₂O₃ catalysts on the kinetics of the hydrodenitrogenation of methylcyclohexylamine were investigated. The catalysts were prepared from ammonium tetrathiotungstate and fully sulfided. The kinetic data were obtained by varying the initial reactant partial pressure and the reaction temperature, and a Langmuir-Hinshelwood kinetic model was used to fit the data. The hydrodenitrogenation of methylcyclohexylamine takes place via two mechanisms, ammonia elimination to methylcyclohexene, and nucleophilic substitution by SH followed by hydrogenolysis of the C–S bond of methylcyclohexyl mercaptan to methylcyclohexane. The first mechanism has a higher activation energy than the second. Addition of nickel changes the nature of the site for the elimination; it increases the activation energy of the reaction and the equilibrium adsorption constant of the reactant on the active site. Fluorination does not change the intrinsic properties of the active sites, but it decreases the number of the active sites.

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Key Words: HDN; fluorination; nickel; WS₂/Al₂O₃; kinetics; methylcyclohexylamine.

1. INTRODUCTION

Removal of nitrogen from oil fractions is an important objective for hydrotreating processes. Breaking of different kinds of C–N bonds is an essential step in accomplishing this task. According to the type of carbon atom to which the nitrogen atom is bonded, there are two kinds of C–N bonds: C(sp²)–N, like in aniline, and C(sp³)–N, like in cyclohexylamine. The active site for C(sp³)–N bond breaking differs from the site for C(sp²)–N bond breaking (1–3). The hydrodenitrogenation (HDN) of aniline-type molecules (e.g., ortho-propylaniline, which is an intermediate in the HDN of quinoline) goes preferentially via hydrogenation of the phenyl ring (4–7); thus, eventually the N atom is removed via C(sp³)–N bond breaking. Nevertheless, only few HDN studies are concerned with C(sp³)–N bond breaking (2, 7–9).

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The promotive effect of fluorine on HDN over W/Al₂O₃ or Mo/Al₂O₃ catalysts was investigated with pyridine (10, 11). Conversion of pyridine involves hydrogenation of the heterocyclic ring and C–N bond breaking, but these steps have not been studied separately. In most cases, the hydrogenation step and the subsequent C–N bond breaking have a similar rate (4, 12–14). Consequently, it was not clear whether the effect of catalyst modification on the HDN of pyridine arose from both reaction steps or only from one of them. We investigated the effect of fluorine on the elementary reactions involved in the HDN of *o*-toluidine and methylcyclohexylamine (MCHA) over W/Al₂O₃ catalysts, and found that fluorine increased the activity of the hydrogenation of the aromatic ring and the breaking of the C(sp²)–N bond, while it hardly affected the HDN of MCHA and the hydrogenation of methylcyclohexene (15). The HDN of MCHA over NiMo/Al₂O₃ has been proposed to take place via two mechanisms (Fig. 1): a Hofmann-type elimination (path 1) and a nucleophilic substitution (path 2) (7). Analysis of the data obtained from the HDN of MCHA over tungsten-based catalysts showed that fluorine slightly increased the elimination and decreased the substitution (15).

The incorporation of nickel in molybdenum (or tungsten) catalysts is traditionally considered to promote the hydrogenation activity (16, 17). It was also found that addition of nickel to tungsten catalysts increased the activity for the HDS of thiophene (18, 19). Reports of the effect of nickel on C–N bond breaking are scarce. Jian *et al.* found that introduction of nickel to Mo/Al₂O₃ catalysts accelerated the C–N bond breaking of piperidine (14) and decahydroquinoline (8). To better understand the effects of fluorine and nickel on C(sp³)–N bond breaking, a kinetic investigation of the HDN of MCHA over tungsten catalysts was conducted in the present study.

Kinetic data can only be interpreted meaningfully if the catalyst consists of a single phase. Classically prepared alumina-supported tungsten catalysts are only partially sulfided, however (20–24). Thus, introduction of fluorine and nickel to classically prepared W/Al₂O₃ catalysts will affect the proportions of the WS₂ active phase and the nonsulfided

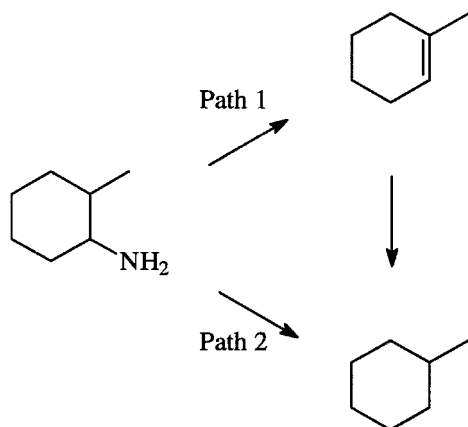


FIG. 1. HDN network of MCHA.

species. Consequently, it is difficult to clarify the promotional effect of fluorine and nickel on the WS₂ active phase. Fully sulfided tungsten catalysts were obtained by using ammonium tetrathiotungstate (ATT) as the precursor (23, 24), and such catalysts have been used in the present study.

2. EXPERIMENTAL

Details of the preparation of tungsten-only (ATT/Al₂O₃ and ATT/Al₂O₃-F) (23) and nickel-promoted (Ni-ATT/Al₂O₃ and Ni-ATT/Al₂O₃-F) (24) catalysts were reported before. All the catalysts contained 10 wt% of tungsten; the nickel-promoted catalysts contained 1 wt% of nickel, and the fluorine content in the fluorinated catalysts was 1 wt%. Prior to HDN reaction, the catalysts were treated *in situ* with a mixture of H₂S (10 mol%) and H₂ (90 mol%) at 400°C and 1.5 MPa for 4 h. Then, the temperature was lowered to 370°C, the pressure was increased to 3.0 MPa, and the liquid feed was introduced to the reactor by means of a high-pressure pump, with *n*-octane as solvent and *n*-heptane as internal standard. Dimethyldisulfide was added to the feed to generate H₂S (6 kPa) in the reaction stream. The partial pressure of MCHA varied from 2 to 21 kPa, while the partial pressures of *n*-octane and *n*-heptane were kept constant at 67 and 8 kPa, respectively. The partial pressure of H₂ varied slightly from 2890 to 2910 kPa, to keep the total pressure constant at 3.0 MPa.

3. RESULTS

Influence of Partial Pressure of MCHA

Under the same reaction conditions, the conversion of MCHA decreases with increasing initial partial pressure of MCHA because of self-inhibition. As an example, Fig. 2 gives the conversion of MCHA at different initial partial pressures on the ATT/Al₂O₃, Ni-ATT/Al₂O₃ and Ni-ATT/Al₂O₃-F catalysts as a function of weight time.

Addition of fluorine and nickel to the catalyst may affect the strength of adsorption of MCHA as well as its reactivity. As a consequence, the partial pressure of MCHA in the feed may influence the apparent relative activity of the catalysts. Figure 2 shows that nickel and fluorine did not have significant effect on the conversion of MCHA at high partial pressure of MCHA, while nickel increased and fluorine decreased the conversion of MCHA at low partial pressure. At high partial pressure of MCHA, the active sites of both catalysts are fully covered by the reactant, and the difference in adsorption constants does not have a significant influence on the apparent activity. At low partial pressure, however, the active sites are only partially covered by the reactant, and a larger adsorption constant gives a higher coverage and thus a relatively higher apparent activity. Comparison of the Ni-ATT/Al₂O₃-F and ATT/Al₂O₃ with ATT/Al₂O₃-F gave the same result about the effect of nickel and fluorine (not shown). This indicates that nickel increases and fluorine decreases the adsorption constant of MCHA, which was confirmed by the kinetic calculations (see below).

Influence of Reaction Temperature

If the activation energy for the HDN of MCHA on one catalyst differs from that on another, the apparent relative activities of the catalysts should change with reaction temperature. Figure 3 shows that the activity of the Ni-ATT/Al₂O₃-F catalyst is slightly lower than that of the ATT/Al₂O₃-F catalyst at 320°C, the same at 345°C, but higher at 370°C. Reaction temperature does not

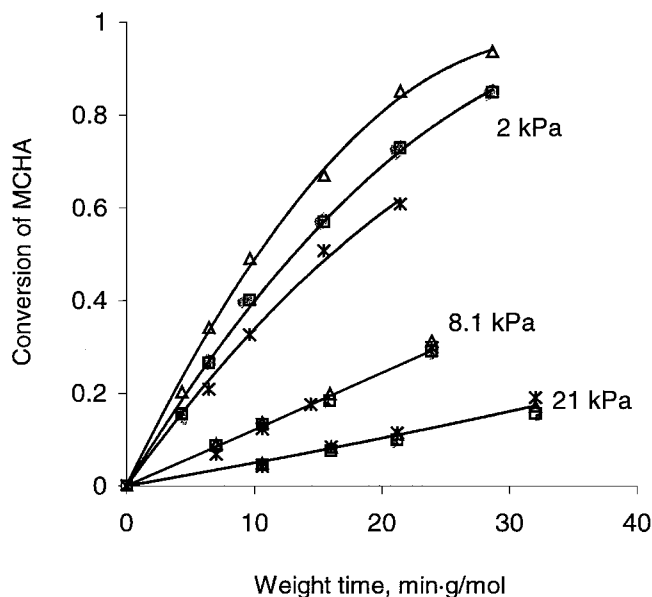


FIG. 2. Comparison of the apparent activities of Ni-ATT/Al₂O₃ (Δ), Ni-ATT/Al₂O₃-F (□), and ATT/Al₂O₃ (*) in the HDN of MCHA at 320°C and 3.0 MPa for different partial pressures of MCHA in the feed.

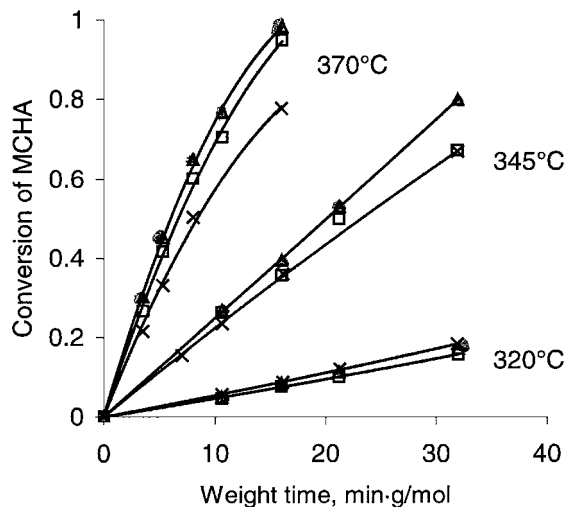


FIG. 3. Comparison of the apparent activities of Ni-ATT/Al₂O₃ (Δ), Ni-ATT/Al₂O₃-F (□), and ATT/Al₂O₃-F (×) in the HDN of MCHA at different temperatures (21 kPa MCHA, 3.0 MPa).

change the relative activities of the fluorine-containing and fluorine-free Ni-ATT/Al₂O₃ catalysts significantly. This indicates that the reaction over the Ni-ATT/Al₂O₃-F catalyst has a higher activation energy than over the ATT/Al₂O₃-F catalyst, while fluorination does not affect the activation energy to a significant extent.

The HDN of MCHA proceeds according to a Hofmann-type elimination, which gives methylcyclohexene (MCHE) as the product, and according to a nucleophilic substitution, which gives methylcyclohexane (MCH) as the product (Fig. 1) (7, 15). In the presence of MCHA, the hydrogenation of MCHE to MCH does not proceed to a significant extent due to the strong inhibition effect of MCHA on the hydrogenation (15). As a consequence, the selectivity of MCHE is almost independent of the conversion of MCHA up to high MCHA conversion (Fig. 4). The selectivities of MCHE and MCH thus reflect the relative reaction rates of these two mechanisms, elimination and substitution. Figure 5 shows the influence of the reaction temperature on the selectivity of MCHE in the HDN of MCHA over the Ni-ATT/Al₂O₃ and ATT/Al₂O₃ catalysts. The selectivity of MCHE is higher at 370°C than at 320°C, indicating that the elimination mechanism has a higher activation energy than the substitution mechanism. The increase in selectivity of MCHE with temperature is higher for the Ni-ATT/Al₂O₃ catalyst than for the ATT/Al₂O₃ catalyst, meaning that the difference in activation energy between these two mechanisms is larger for the former catalyst than for the latter.

Kinetic Parameters

The Langmuir-Hinshelwood model has often been used to express the kinetics of the HDN reactions occurring on sulfide catalysts (6, 8, 25–27). The kinetic parameters

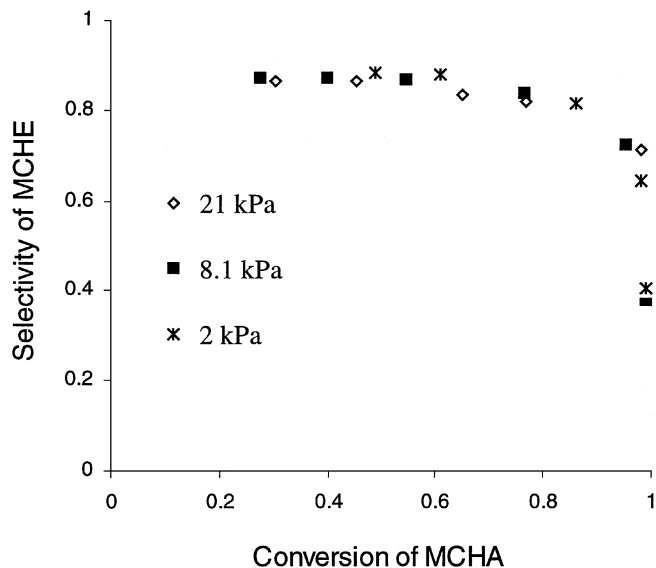


FIG. 4. Influence of the initial partial pressure of MCHA on the selectivity of MCHE (Ni-ATT/Al₂O₃, 370°C, 3.0 MPa).

of the studied catalysts for the HDN of MCHA were obtained by simulating the experimental data with Langmuir-Hinshelwood rate expressions. The HDN of MCHA proceeds along two pathways (Fig. 1). Therefore, the overall HDN conversion is the sum of the two reactions. Reaction conditions and catalyst composition can change the relative concentrations of MCH and MCHE in the HDN product of MCHA, indicating that the active sites for these two mechanisms are different (7, 15). In the Langmuir-Hinshelwood equation, the two pathways then require their own rate as well as adsorption constants. However, a change in the initial partial pressure of MCHA did

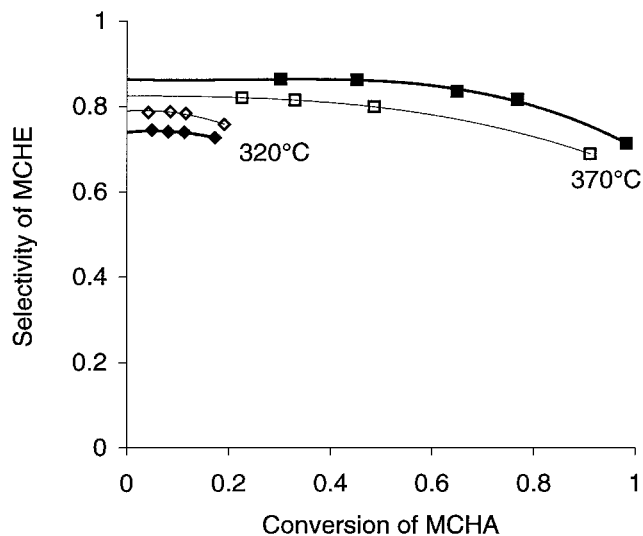


FIG. 5. Effect of the reaction temperature on the selectivity for MCHE of Ni-ATT/Al₂O₃ (heavy line) and of ATT/Al₂O₃ (thin line) in the HDN of MCHA (21 kPa MCHA, 3.0 MPa).

not affect the selectivity of MCHE to a significant extent (Fig. 4), indicating that the adsorption constants of MCHA on the two sites are equal. Therefore, it is possible to simplify the Langmuir-Hinshelwood equation by using one and the same adsorption constant for both sites. The adsorption of the N-free products on the active site is much weaker than MCHA and ammonia. Thus,

$$\frac{dP_{\text{MCHA}}}{d\tau} = -\frac{(k_1 + k_2)K_{\text{MCHA}}P_{\text{MCHA}}}{1 + K_{\text{MCHA}}P_{\text{MCHA}} + K_{\text{NH}_3}P_{\text{NH}_3}} \quad [1]$$

$$P_{\text{NH}_3} = P_{\text{MCH}} + P_{\text{MCHE}}, \quad [2]$$

where τ is the weight time, k_1 and k_2 are the rate constants for path 1 and path 2, respectively, K_{MCHA} and K_{NH_3} are the adsorption constants of MCHA and NH₃, respectively, and P_{MCHA} , P_{NH_3} , P_{MCH} , and P_{MCHE} are the partial pressures of MCHA, NH₃, MCH, and MCHE, respectively. Results of the nonlinear regression of the experimental data according to Eqs. [1] and [2] showed that K_{NH_3} was about an order of magnitude smaller than K_{MCHA} , and that its standard deviation was large. Therefore, the adsorption of ammonia was ignored and Eq. [1] simplified to

$$\frac{dP_{\text{MCHA}}}{d\tau} = -\frac{(k_1 + k_2)K_{\text{MCHA}}P_{\text{MCHA}}}{1 + K_{\text{MCHA}}P_{\text{MCHA}}}. \quad [3]$$

Direct simulation of the partial pressure of MCHA versus weight time with the above equation did not give unique parameter values. The experimental data fitted the model equally well with a variety of combinations of $(k_1 + k_2)$ and K_{MCHA} . To get unique parameters one of the parameters must be determined independently, as Jian and Prins already pointed out before (6, 8). At large partial pressure of MCHA, $K_{\text{MCHA}}P_{\text{MCHA}} \gg 1$, and Eq. [3] simplifies to

$$X_{\text{MCHA}} = \frac{k_1 + k_2}{P_{\text{MCHA}}^0} \cdot \tau, \quad [4]$$

where X_{MCHA} is the conversion of MCHA and P_{MCHA}^0 is the initial partial pressure of MCHA. As an example, Fig. 6 gives the conversions of MCHA over the Ni-ATT/Al₂O₃ catalyst versus weight time when the initial partial pressure of MCHA is 21 kPa. The very good linearity

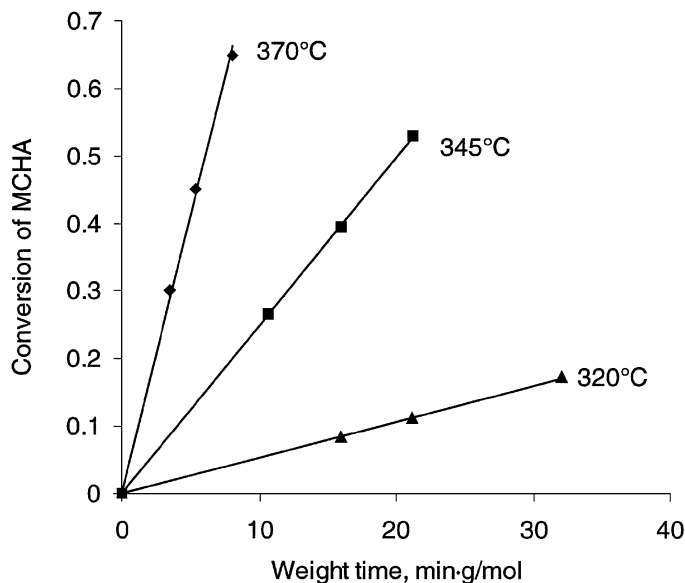


FIG. 6. Conversion versus weight time in the HDN of MCHA over Ni-ATT/Al₂O₃ (21 kPa MCHA, 3.0 MPa).

of the plots indicates that the above simplification is justified. Thus, the sums of k_1 and k_2 were obtained for all catalysts, and the results are given in Table 1. Once $k_1 + k_2$ was determined, the adsorption constant K_{MCHA} could be determined uniquely by varying the initial partial pressure of MCHA from 2 to 21 kPa and by nonlinear regression analysis of the experimental data according to Eq. [3]. The results are also presented in Table 1. Figure 7 presents the experimental data for three different initial partial pressures of MCHA and the simulation results (drawn lines) for the Ni-ATT/Al₂O₃ catalyst. The statistical evaluation of the goodness-of-fit gave the standard deviations of the parameters, which are also presented in Table 1 (in parentheses).

Figure 4 shows that the selectivity of MCHE is constant when the conversion of MCHA is lower than 50%. At low conversion of MCHA, path 1 and path 2 constitute parallel reactions (7, 15), and the selectivities of MCHE and MCH at low conversion of MCHA are equal to $k_1/(k_1 + k_2)$ and

TABLE 1

Kinetic Parameters Obtained by Fitting the Conversion of MCHA at 3.0 MPa with a Langmuir-Hinshelwood Expression, $k_1 + k_2$ in $\text{kPa} \cdot \text{mol} \cdot \text{min}^{-1} \cdot \text{g}^{-1}$, K_{MCHA} in kPa^{-1}

		ATT/Al ₂ O ₃	ATT/Al ₂ O ₃ -F	Ni-ATT/Al ₂ O ₃	Ni-ATT/Al ₂ O ₃ -F
370°C	$k_1 + k_2$	1.44 (0.03)	1.47 (0.03)	1.79 (0.03)	1.64 (0.03)
	K_{MCHA}	0.49 (0.05)	0.27 (0.02)	0.61 (0.07)	0.60 (0.06)
345°C	$k_1 + k_2$	0.47 (0.01)	0.47 (0.01)	0.53 (0.01)	0.46 (0.01)
	K_{MCHA}	0.72 (0.10)	0.47 (0.08)	1.17 (0.34)	0.99 (0.26)
320°C	$k_1 + k_2$	0.113 (0.004)	0.113 (0.004)	0.111 (0.001)	0.100 (0.001)
	K_{MCHA}	1.06 (0.25)	0.60 (0.15)	3.0 (0.4)	2.1 (0.2)

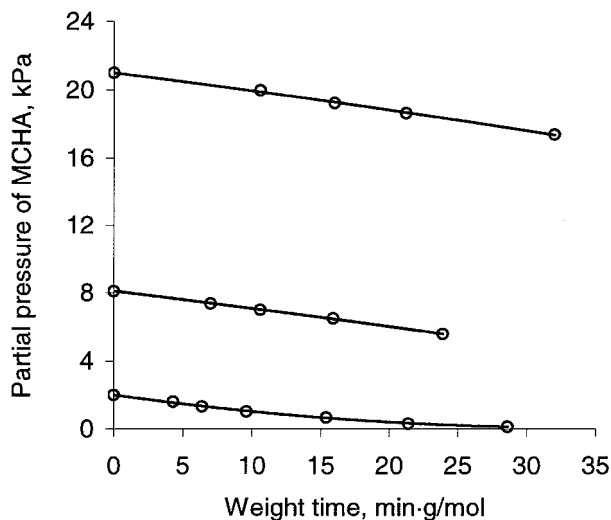


FIG. 7. Comparison of the experimental data (points) and model prediction results (lines) for the HDN of MCHA over the Ni-ATT/Al₂O₃ at 320°C and 3.0 MPa with three initial partial pressures.

$k_2/(k_1 + k_2)$, respectively. Thus, the ratio of k_1 to $k_1 + k_2$ and the individual values of k_1 and k_2 can be obtained, and they are given in Table 2.

The activation energies of the HDN reaction paths 1 and 2 for the studied catalysts were obtained according to the Arrhenius equation. The results are given in Table 3. The standard deviations in parentheses were obtained through a statistical calculation using the MicroMath Scientist program. Similarly, the heats of adsorption of MCHA and their standard deviations were calculated and are given in Table 4. As an example, Fig. 8 gives the plots of the temperature dependence of the rate constants of paths 1 and 2 and of the equilibrium adsorption constant of MCHA on the Ni-ATT/Al₂O₃ catalyst.

4. DISCUSSION

The elimination of ammonia from MCHA is the major path in the HDN of MCHA over the WS₂/Al₂O₃ catalysts

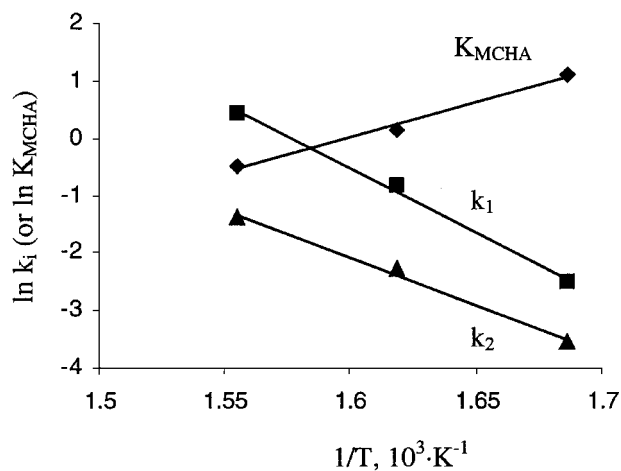


FIG. 8. Temperature dependence of the rate constants of path 1 (k_1) and path 2 (k_2) and the equilibrium adsorption constant of MCHA for the HDN of MCHA over the Ni-ATT/Al₂O₃ catalyst at 3.0 MPa.

(Figs. 4 and 5), and it is affected to a greater extent by addition of nickel and fluorine than the substitution path (Table 2). The change in the total conversion of MCHA caused by catalyst modification is mainly due to the change in activity for the elimination path. The activation energy of the elimination reaction (path 1) is higher than that of the substitution reaction (path 2) for all catalysts studied (Table 3), indicating that the elimination mechanism is relatively favored at higher reaction temperatures. This explains why the selectivity of MCHE is higher at 370°C than at 320°C (Fig. 5).

The sites for these two reactions are different in nature. The two nickel-containing catalysts have significantly higher activation energies for the elimination reaction than the two nickel-free catalysts, while the fluorine-containing and fluorine-free catalysts show no difference in activation energy (Table 3). The same is true for the heat of adsorption of MCHA on the active sites (Table 4). These results indicate that the addition of nickel to the tungsten catalyst changes the nature of the active sites whereas

TABLE 2

Rate Constants of the Paths 1 and 2 for the HDN of MCHA at 320 to 370°C, 3.0 MPa over Different Catalysts (kPa · mol · min⁻¹ · g⁻¹)

		ATT/Al ₂ O ₃	ATT/Al ₂ O ₃ -F	Ni-ATT/Al ₂ O ₃	Ni-ATT/Al ₂ O ₃ -F
370°C	$k_1/(k_1 + k_2)$	0.82	0.88	0.86	0.89
	k_1	1.18	1.29	1.54	1.46
	k_2	0.26	0.18	0.25	0.18
345°C	$k_1/(k_1 + k_2)$	0.80	0.86	0.81	0.85
	k_1	0.38	0.40	0.43	0.39
	k_2	0.09	0.07	0.10	0.07
320°C	$k_1/(k_1 + k_2)$	0.79	0.84	0.74	0.81
	k_1	0.089	0.095	0.082	0.081
	k_2	0.024	0.018	0.029	0.019

TABLE 3

Arrhenius Constants in the HDN of MCHA at 3.0 MPa, $k = A \cdot \exp(-Ea/RT)$

	ATT/Al ₂ O ₃	ATT/Al ₂ O ₃ -F	Ni-ATT/Al ₂ O ₃	Ni-ATT/Al ₂ O ₃ -F
Path 1				
<i>Ea</i> (kJ/mol)	164 (7)	166 (7)	186 (10)	184 (5)
<i>A</i> (kPa · mol ⁻¹ · g ⁻¹)	3E + 13	4E + 13	1E + 15	1E + 15
Path 2				
<i>Ea</i> (kJ/mol)	151 (10)	146 (8)	137 (9)	143 (10)
<i>A</i> (kPa · mol ⁻¹ · g ⁻¹)	6E + 11	1E + 11	3E + 10	8E + 10

fluorine does not affect the intrinsic properties of the sites. Elimination of ammonia from MCHA requires a pair of basic and acidic sites. The basic site can be a surface sulfur atom and the acidic site a neighboring sulfur vacancy or an SH group attached to a sulfided tungsten atom. It is believed that nickel and tungsten in the sulfided catalyst form the Ni-W-S structure (18, 19, 28, 29). The nature of the surface sulfur atom, sulfur vacancy, and SH group on the Ni-W-S structure differs from that on the WS₂ structure (30, 31). The activation energy of the elimination reaction is larger (Table 3), and the adsorption of MCHA is stronger (Table 4) on the Ni-W-S sites than on the WS₂ sites. Although fluorination of the alumina support affects the dispersion and sulfidation of molybdenum (32–34) and tungsten (10, 11, 23, 24, 35), there is no evidence that fluorine changes the structure of the active phase. The fact that fluorine did not change the activation energy and the heat of the adsorption of MCHA on the active site excludes a change in nature of the sites induced by fluorination. Our catalysts were prepared from ATT and shown to be fully sulfided (23, 24), therefore, fluorine mainly changed the size and the stacking of the WS₂ slabs (10, 23, 24, 36). The change in the morphology of the catalyst surface induced by fluorination may affect the entropy change for the adsorption of MCHA. At one temperature, the heat of adsorption and the change in entropy together determine the adsorption constant. Fluorination did not change the heat of adsorption, but it decreased the adsorption constant moderately. The moderate change in the adsorption constant may be ascribed to an entropy effect.

All the catalysts have similar activation energies for reaction 2 (Table 3), meaning that the incorporation of nickel

and fluorine did not change the nature of the site for the substitution. However, fluorine decreased the rate constant of path 2 (k_2), while nickel had no influence on k_2 . The number of the active sites and their intrinsic activity determine the rate constant. Therefore, it is concluded that fluorine does not change the intrinsic properties of the site for substitution reaction, but decreases the number of the sites, and that nickel has no influence on the substitution mechanism. The substitution reaction is catalyzed by surface SH groups created by dissociative adsorption of H₂S on the catalyst surface (7). Fluorination of the alumina support leads to a poorer dispersion of tungsten (10, 11, 15, 35); thus there are fewer surface tungsten atoms to dissociate H₂S. That nickel has no influence on the substitution reaction indicates that the active site for the substitution mechanism is only related to the surface SH groups, and that Ni has no influence on their number and properties.

For heterogeneous catalytic reactions, the apparent activity of a catalyst is determined by the rate constant (product of the number of active sites and their intrinsic activity) and the coverage of the reactant (determined by equilibrium adsorption constant and partial pressure of the reactant). Two catalysts with different adsorption constants may exhibit different relative activities when using feeds with different partial pressures of reactant. Figure 2 shows that the reaction rate of the HDN of MCHA is larger over the Ni-ATT/Al₂O₃ catalyst than over the ATT/Al₂O₃ catalyst when using a low concentration feed, but it is smaller when using a high concentration feed. Therefore, one cannot simply say that the effect of nickel on the HDN of MCHA is positive or negative. It is necessary to perform a kinetic investigation to reveal the effect of the catalyst modification on the nature of the active sites.

TABLE 4

Temperature Dependence of $K_{\text{MCHA}} = K_0 \cdot \exp(-\Delta H/RT)$ at 3.0 MPa

	ATT/Al ₂ O ₃	ATT/Al ₂ O ₃ -F	Ni-ATT/Al ₂ O ₃	Ni-ATT/Al ₂ O ₃ -F
$-\Delta H$ (kJ/mol)	49 (1)	50 (12)	101 (9)	80 (7)
K_0 (kPa ⁻¹)	5E - 5	2E - 5	4E - 9	2E - 7

5. CONCLUSION

The apparent activity cannot fully reflect the effect of catalyst modification on the catalytic performance. The apparent activity depends on the reaction conditions and feed composition. A kinetic investigation can reveal a change in nature of the active sites. Incorporation of nickel in the tungsten catalyst affects the intrinsic properties of the active site for the elimination of ammonia from MCHA, while it has no effect on the nature of the site for the substitution of NH₂ by SH in MCHA. Fluorine does not change the intrinsic properties of the active sites, but it changes the dispersion of the active sites on the surface. The change in the morphology of the surface affects the entropy of the adsorption of MCHA, and thus moderately influences the adsorption constant of MCHA.

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