Kinetic approach of surface acidity of W_2N, Mo_2N and NbN catalysts using methylbutynol as molecular probe

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Abstract

In order to get more information on the acidic sites of early transition metal nitrides, methylbutynol (2-methylbut-3-yn-2-ol) (MBOH) conversion was performed on bulk W_2N, NbN and Mo_2N passivated by oxygen after synthesis. The reaction proceeds through two parallel routes leading either to 2-methylbut-1-en-3-yne (Mbyne) by dehydration, or to 3-methylbut-2-enal (prenal) by isomerisation. Deactivation during time on stream occurred for both routes, the selectivity remaining constant. This deactivation can be modelled by a second-order rate law allowing to give accurate initial reaction rates. Zero-order reactions were shown to occur, leading to constant reaction rates along the two routes: $r_{Mbyne} = 3.71 \times 10^{-4} \, \text{mol} \, \text{min}^{-1} \, \text{g}^{-1}$ and $r_{prenal} = 1.94 \times 10^{-4} \, \text{mol} \, \text{min}^{-1} \, \text{g}^{-1}$ in the case of W_2N. Similar global activation energies were also found for both ways: $E_{a, Mbyne} = 24.7 \, \text{kJ} \, \text{mol}^{-1}$ and $E_{a, prenal} = 22.1 \, \text{kJ} \, \text{mol}^{-1}$. All these data were interpreted in terms of acidic hydroxyl and metal-oxo groups, linked to the same surface transition metal atom. Dehydration occurs on Brönsted acid sites, whereas isomerisation occurs on metal-oxo ones. Kinetic coupling of two catalytic cycles, linked by the same elementary step (MBOH chemisorption), leads to the saturation of all surface active sites by the reactant, with two different turnover rates. This kinetic model permitted a coherent interpretation of all the data. The differences observed between W_2N, NbN and Mo_2N are interpreted in terms of acid–base properties of the catalytic materials.
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Keywords: Molybdenum; Tungsten and niobium nitrides; Acidic properties; 2-Methylbut-3-yn-2-ol molecular probe; Kinetic coupling.

1. Introduction

In recent years it has been shown that oxygen-containing carbides and nitrides of early transition metals (Mo, W, Nb, Ti, ...) exhibit bifunctionnal properties for some catalytic reactions [1–4] implying the association of metallic and acidic sites. Metallic sites of these materials have been much more studied than acidic ones. Several methods are commonly used to determine the acidity (type, strength, number of sites) of solid acid catalysts, such as adsorption of probe molecules (NH_3, pyridine), IR spectroscopy of these molecular probes, titration methods or molecular probe reactions [5]. If many of these techniques are used for solid oxides, very few studies have been performed yet about the determination of acid–base properties of nitrides. The presence of Brönsted and Lewis acid sites has been evidenced by pyridine adsorption monitored by diffuse reflectance FTIR over

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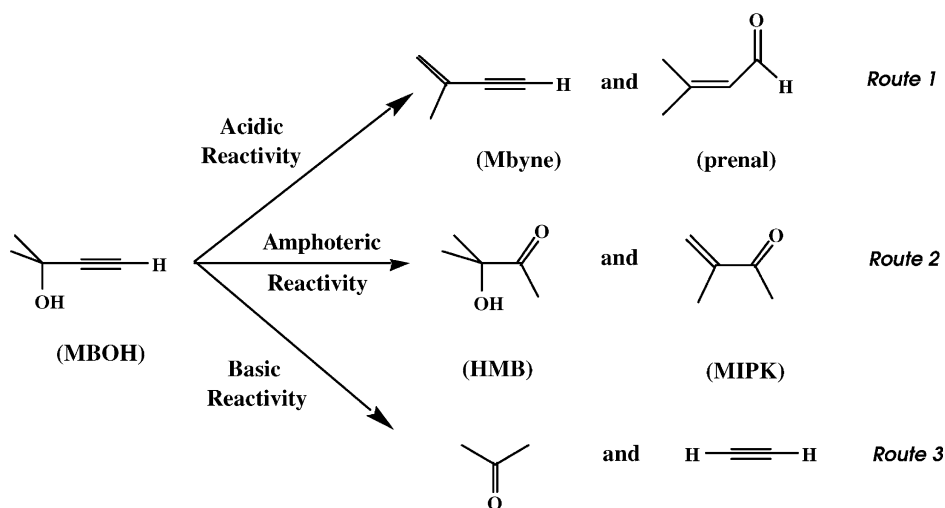
Fig. 1. Three different pathways for MBOH conversion.

nitrided catalysts such as molybdenum species [6]. Furthermore, basic sites have been evidenced on aluminovanadate oxynitride [7]. The use of a catalytic probe reaction is generally a good tool to reveal the acid–base properties of a solid in real catalytic conditions. The conversion of a secondary alcohol is very often used to evaluate simultaneously the acidic and basic properties of solids. But if the dehydration activity of the alcohol occurs on acidic sites, the dehydrogenation to a ketone can also be related to either the basic or redox properties of the material [8]. This is why a new molecule has been proposed [9]: the 2-methylbut-3-yn-2-ol (MBOH), the simplest tertiary alkynol. It has been shown to be a sensitive molecular probe to evaluate acidic and basic sites of solid oxides [9] and has already been used to characterise different kinds of catalysts [10–17]. Reaction pathways are reported in Fig. 1: on acidic catalysts, MBOH undergoes both dehydration and isomerisation to yield 2-methylbut-1-en-3-yne (Mbyne) and 3-methylbut-2-enal (prenal), respectively, on basic surfaces, MBOH leads to acetone and acetylene. MBOH may also be a probe for amphoteric catalysts by hydration to 3-hydroxy-3-methylbutan-2-one (HMB) and isomerisation to 3-methylbut-3-en-2-one (MIPK). These different routes have been proposed in the first publication on the subject [9]. The other works [10–17] concerning mainly the reactivity toward acetone and acetylene (basic sites) and toward

Mbyne (acidic sites) corroborate the initial conclusion. The isomerisation to prenal has always been obtained on acidic materials [9]. Moreover, it is well known either in homogenous organometallic catalysis [28], or in heterogenous catalysis [29] that metalloxo active sites are involved in such a reaction. This probe reaction is thus claimed to be a versatile and sensitive tool for the characterisation of the acid–base properties of inorganic solids.

The aim of the present paper is to evidence which route(s) (1, 2 or 3, Fig. 1) can occur over W_2N, Mo_2N, NbN and to evaluate the influence of the nature of the transition metal on the corresponding acid–base properties. The effect of the reduction of passivated nitrides was also investigated.

2. Experimental

2.1. Materials

W_2N ($S_g = 39 \, m^2 \, g^{-1}$, as determined by B.E.T. method on a Quantachrome-Quantasorb Jr.) [18], Mo_2N ($S_g = 35 \, m^2 \, g^{-1}$) [19] and NbN ($S_g = 42 \, m^2 \, g^{-1}$) [4] were prepared according to methods already described in the literature [20]. After preparation catalysts were passivated by flowing 1 vol.% O_2/He at room temperature, in order to avoid bulk oxidation.

2.2. Reactor device—standard run procedure

Experiments were performed in an automated differential flowing microreactor. The feed consisted of MBOH in helium, obtained by bubbling helium (20 cm^3 min^{-1}) in liquid MBOH at 20 °C and resulting in a MBOH partial pressure of 1.73 kPa [21]. This partial pressure was changed from 0.89 to 3.18 kPa for determining the reaction order. Catalyst sample (about 20 mg) was located in the centre of a tubular quartz reactor of 30 cm long and 3 mm i.d. In a "standard run", a catalyst passivated by oxygen after preparation, was pre-treated in flowing H$_2$ (20 cm^3 min^{-1}) at 773 K, for 1 h. Flowing N$_2$ (20 cm^3 min^{-1}) at 773 K was then proceeded to remove adsorbed hydrogen so that it could not further hydrogenate the reactant. The temperature of reactor was then decreased to the desired value (in the range 388–453 K). Reaction products were analysed at different times on stream using a GIRA gas chromatograph equipped with a flame ionisation detector. The packed column which contained 15% TCEPE on Silocel separated all the components.

2.3. Conversion and selectivity

Data are given in terms of conversion and selectivity. The partial pressure of each product P_i was calculated from chromatographic measurements by using the appropriate response coefficient and the value of the initial partial pressure of MBOH in the feed, P^0_{MBOH}.

Mbyne and prenal were the only products detected and the global selectivity in each product S_i is defined as:

$$S_i(\%) = \frac{P_i}{\sum P_i} 100$$

The conversion τ can be expressed as:

$$\tau(\%) = \frac{P^0_{\mathrm{MBOH}} - P_{\mathrm{MBOH}}}{P^0_{\mathrm{MBOH}}} 100$$

But as deactivation was readily occuring on catalysts, another definition has to be used:

$$\tau^e(\%) = \frac{\sum P_i^e}{P^0_{\mathrm{MBOH}}} 100$$

where P_i^e is the partial pressure of the i product extrapolated at time on stream equal to zero, as explained in Section 3.1.

3. Results

In Sections 3.1 and 3.2, the reaction of MBOH was only performed on W$_2$N. Criteria of Koros and Nowak [22] were verified: changing the mass of catalyst and the reactant flow without modifying the contact time did not change the catalytic results. So no diffusion phenomenon was observed in our experimental conditions. Only route 1 (Fig. 1), leading to Mbyne and prenal, was observed, revealing the acidic character of the surface of W$_2$N. The properties responsible for the selectivities toward Mbyne and prenal will be discussed later.

3.1. Catalyst deactivation-regeneration: extrapolated results

The catalytic results for a standard run on W$_2$N are given in Fig. 2. The first minutes on stream showed a strong deactivation of the catalyst but the selectivity remained constant during the whole catalytic run (about 40 min). It was possible to partially regenerate the initial catalyst activity: a new treatment in flowing H$_2$ at 673 K leads to a recovering of the conversion from 6 (Fig. 2 after 42 min of run) to 61% instead of 67% for the first run (Fig. 2 after 2 min of run). A treatment by N$_2$ at 673 K after run was also checked, but it was quite less efficient than that by H$_2$. This deactivation can be either due to a strong product adsorption on the surface, leading to a strong inhibition effect on the reaction rate, or to the production of coke on acidic sites, as it has been proposed on other acidic materials [10].

Thus, in order to compare the properties of the different catalysts in this reaction, we had to determine their initial activities. So we tried to modelise the deactivation law and found that for each product, the function $1/P_i$ varied linearly with time on stream (i being either Mbyne or prenal). This plot is reported in Fig. 3.

It shows that the linear law proposed by Germain and Maurel for deactivation [23] fits our data assuming that conversion versus product i is linearly related to
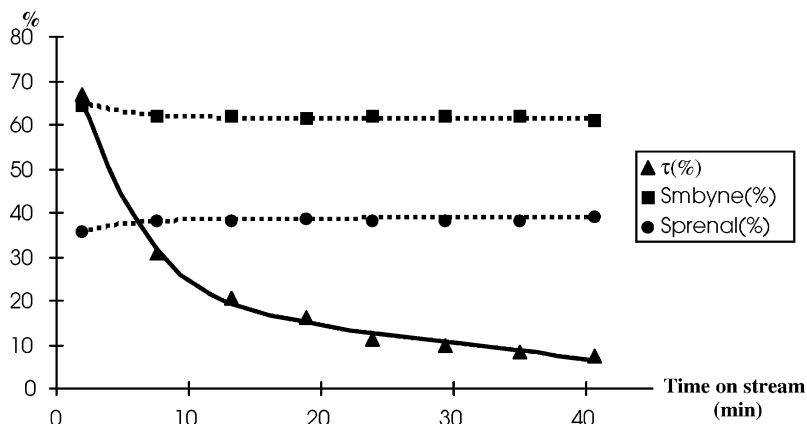
Fig. 2. Standard run on 20.4 mg W_2N at 453 K. Conversion, Mbyne and prenal selectivities vs. time on stream.

its partial pressure P_i (Eq. (1)).

$$\frac{1}{P_i} = \frac{1}{P_i^e} + k_i^d t \tag{1}$$

where P_i is the actual partial pressure of product i, P_i^e the extrapolated partial pressure of product i, k_i^d the deactivation coefficient ($Pa^{-1} s^{-1}$) and t the time on stream (s).

This equation was established by Levenspiel [24] in the hypothesis of a second-order deactivation rate law, for a well-mixed reactor. It was used in some papers to determine the initial catalytic properties of a material in a given reaction [25,26].

We can thus, give for each reaction (production of Mbyne and production of prenal) a deactivation coefficient, respectively:

$$k_{Mbyne}^d = 0.311 \, kPa^{-1} \, min^{-1}$$

$$k_{Mbyne}^d = 0.473 \, kPa^{-1} \, min^{-1}$$

The intersection of the curves given in Fig. 3 with the Y-axis permits to calculate the extrapolated values

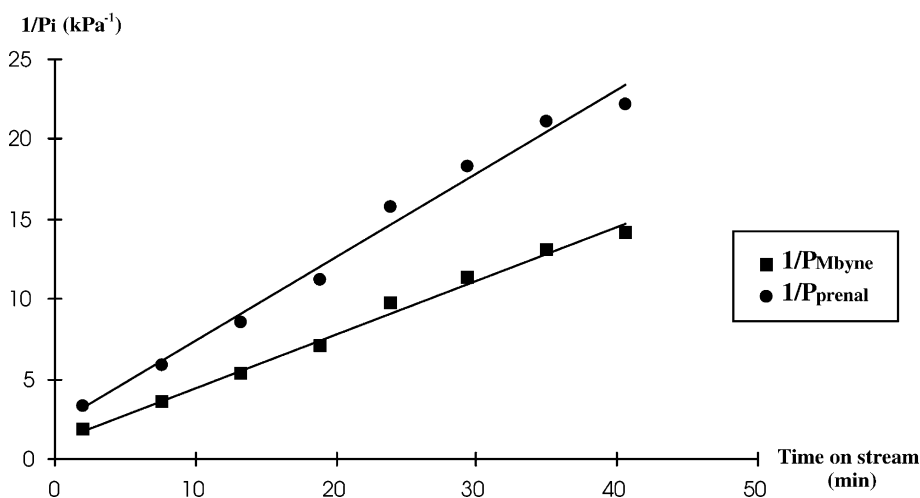Fig. 3. Standard run on 20.4 mg W_2N at 453 K. $1/P_{Mbyne}$ and $1/P_{prenal}$ vs. time on stream.

$P^e_{Mbyne} = 0.818\,kPa$ and $P^e_{prenal} = 0.429\,kPa$. Thus τ^e, S^e_{Mbyne} and S^e_{prenal} can easily be determined:

$$\tau^e(\%) = \frac{\sum P^e_i}{P^0_{MBOH}} 100$$

and

$$S^e_i(\%) = \frac{P^e_i}{\sum P^e_i} 100$$

i being Mbyne or prenal and P^0_{MBOH} being the initial partial pressure of MBOH in the reactant mixture.

In the case of Fig. 3, we have $\tau^e = 72\%$, $S^e_{Mbyne} = 66\%$ and $S^e_{prenal} = 34\%$.

3.2. Effect of pre-treatment

Pre-treatments by H_2 or N_2 for 1 h at 773 K were compared. The curves obtained after a pre-treatment under nitrogen have not been represented. Nevertheless, activation by H_2 yields to conversions higher than the activation by N_2 (67% against 47% after 2 min), although the selectivity to MByne and prenal remained quite similar in both cases. It means that hydrogen is necessary to remove from the surface all the pre-adsorbed oxygen.

So, as seen in Section 2, all catalysts were pre-treated by H_2, then the surface was cleaned by N_2 before run.

Various temperatures of pre-treatment in flowing H_2 were proceeded on W_2N samples for a same reaction temperature of 453 K. Results reported in Table 1 are compared in terms of extrapolated conversions and selectivities.

Table 1
Influence of the pre-treatment temperature on the initial activity and selectivity of W_2N

	Temperature of pre-treatment/H_2			
	613 K	773 K	823 K	873 K
P^e_{Mbyne} (kPa)	0.522	0.818	0.766	0.781
P^e_{prenal} (kPa)	0.324	0.429	0.333	0.338
τ^e (%)	49	72	64	65
S^e_{Mbyne} (%)	62	66	70	70
S^e_{prenal} (%)	38	34	30	30

Catalyst weight: $19.5 \pm 1\,mg$. Reaction temperature: 453 K.

Table 2
Influence of the early transition metal nature on the activity and selectivity of the corresponding nitrides

	Catalyst		
	W_2N	Mo_2N	NbN
P^e_{Mbyne} (kPa)	0.395	0.285	0.144
P^e_{prenal} (kPa)	0.242	0.120	0.040
τ^e (%)	37	23	11
S^e_{Mbyne} (%)	62	70	78
S^e_{prenal} (%)	38	30	22

Weight of catalyst: $19.9 \pm 0.5\,mg$. Reaction temperature: 433 K.

It can be observed that the increase of the temperature pre-treatment in flowing H_2 from 613 to 773 K, leads to higher values of the extrapolated conversions, P^e_{Mbyne} and P^e_{prenal}. Above 773 K, the conversion lowers slightly and the selectivity in prenal becomes smaller.

It can be concluded from these observations that 773 K is sufficient to get the higher total conversion for reactions occurring at 453 K. Moreover, increasing pre-treatment temperatures from 613 to 773 K does not affect the nature of the active sites as far as selectivities in Mbyne and prenal remain at a similar level.

3.3. Comparison of catalytic activities of Mo_2N, W_2N and NbN

The initial values of conversion, partial pressures of Mbyne and prenal, as well as selectivities in Mbyne and prenal are reported in Table 2 for MBOH reactions on Mo_2N, NbN and W_2N. All these materials were tested following the standard procedure at 433 K.

It can be observed that for the same contact time, and for about the same specific areas, the extrapolated conversion of MBOH decreases in the order $W_2N > Mo_2N > NbN$, and the Mbyne extrapolated selectivity increases in the reverse order. To discuss these results and correlate the catalytic performances of the materials to the nature of their active sites, some more kinetic data are necessary to clarify the mechanism of the reaction.

3.4. Mechanistic study

All the experiments described in this section were performed on W_2N catalyst. All the results are given after extrapolation as explained in Section 3.1.

3.4.1. Reaction order

Reaction order related to MBOH was investigated by varying the initial partial pressure of MBOH in the reactant mixture for a given contact time. In Fig. 4 is given the evolution of the partial pressure of MBOH, Mbyne and prenal obtained after extrapolation versus P_{MBOH}^0. We observe that P_{MBOH}^e, can be linearly related to P_{MBOH}^0 with a slope near unity, whereas the slopes obtained for P_{Mbyne}^e and P_{prenal}^e are very small. These experimental results can be fitted by the following kinetic model:

$$\text{MBOH} \begin{array}{c} \nearrow \quad \text{Mbyne} \quad (\mathbf{k_1}) \\ \\ \searrow \quad \text{prenal} \quad (\mathbf{k_2}) \end{array}$$
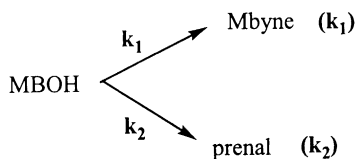
r_1, r_2 and k_1, k_2 being respectively, the reaction rates and the rate constants for Mbyne and prenal formation. Then,

$r_{\text{total}} = r_1 + r_2$, with $r_1 = k_1(P_{MBOH}^e)^{\alpha_1}$

and $r_2 = k_2(P_{MBOH}^e)^{\alpha_2}$

If $\alpha_1 = \alpha_2 = 0$, then $r_1 = k_1$, $r_2 = k_2$

and $r_{\text{total}} = (k_1 + k_2)$

$$P_{\text{Mbyne}}^e = k_1 t \tag{2}$$

$$P_{\text{prenal}}^e = k_2 t \tag{3}$$

$$P_{\text{MBOH}}^e = P^0(\text{MBOH}) - (k_1 + k_2)t \tag{4}$$

These laws fit our data: we find for Eq. (4): $P_{\text{MBOH}}^e = 0.92 P^0(\text{MBOH}) - 0.5$. So we can conclude that each individual reaction as well as the overall conversion of MBOH are zero-order related to MBOH.

Reactions of MBOH were also performed and compared at different contact times. For a given temperature, the total flow was maintained constant ($20\,\text{cm}^3\,\text{min}^{-1}$) and the catalyst weight was changed. The variation of the extrapolated partial pressure of Mbyne and prenal versus catalyst weight (proportional to contact time) at a reaction temperature of 453 K is given in Fig. 5. The curves can be easily fitted by a linear regression as expected for zero-order reactions.

3.4.2. Reaction rates and activation energies

From these results, formation rate of product i can be determined for a given temperature from the slope ($\text{Pa}\,\text{g}^{-1}$) of the curve $P_i^e = f(\text{catalyst weight})$:

$$r_i = \frac{(\text{slope for product } i)F}{P^0} \text{ in mol min}^{-1}\,\text{g}^{-1}$$

where F is the total flow rate ($\text{mol}\,\text{min}^{-1}$) and P^0 the atmospheric pressure (Pa). At 453 K we found:

$r_{\text{Mbyne}} = 3.71 \times 10^{-4}\,\text{mol}\,\text{min}^{-1}\,\text{g}^{-1}$

$r_{\text{prenal}} = 1.94 \times 10^{-4}\,\text{mol}\,\text{min}^{-1}\,\text{g}^{-1}$

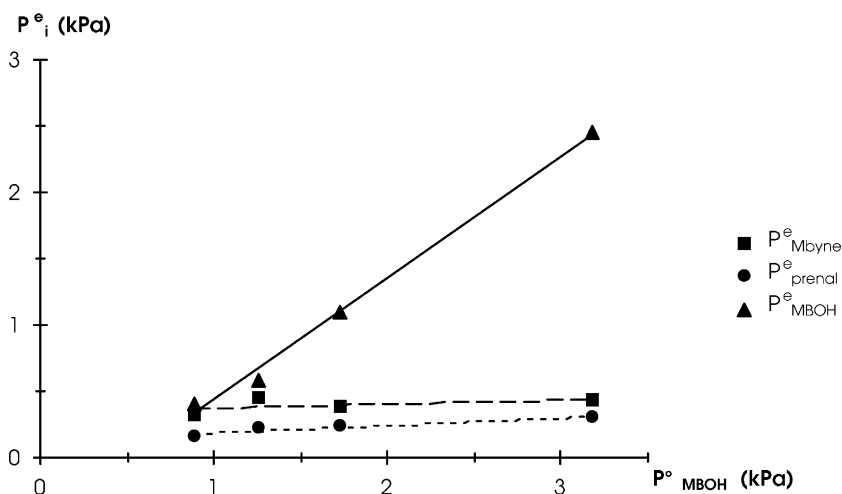Fig. 4. Evolution of the extrapolated partial pressures of MBOH, Mbyne and prenal vs. P_{MBOH}^0. Results obtained on 20 mg W_2N at 433 K.
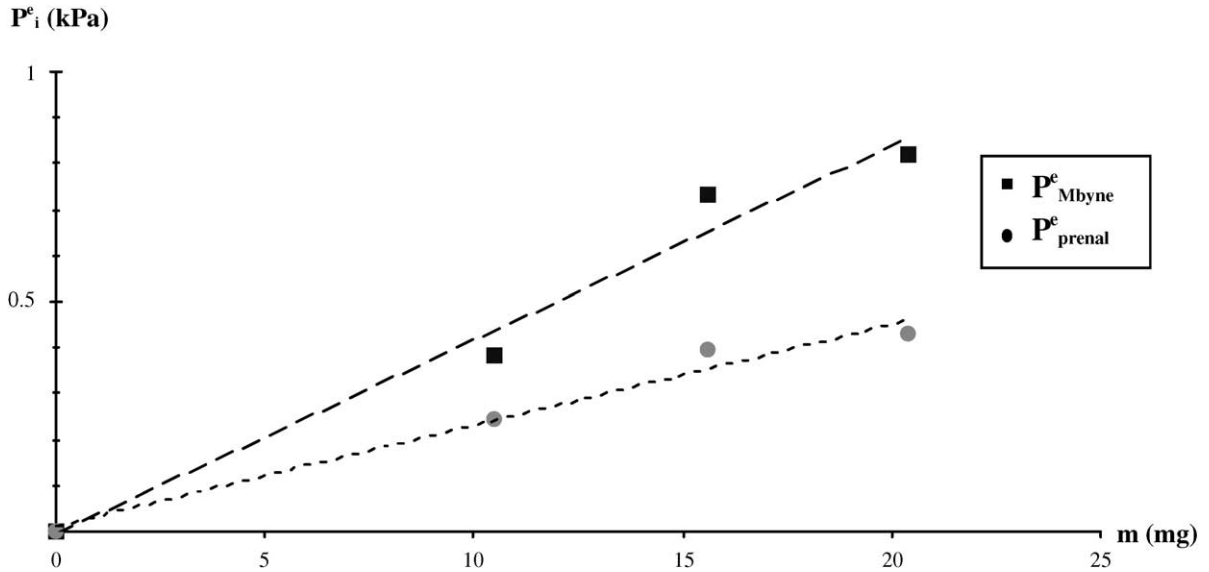
P^e_i (kPa)

Fig. 5. Evolution of the extrapolated partial pressures of Mbyne and prenal vs. catalyst weight. Standard procedure on W_2N at 453 K.

Moreover for three different temperatures, the reaction rates for Mbyne and prenal productions have been determined. Fig. 6 represents the Arrhenius plots ln r versus $1/T$ for Mbyne and prenal. The activation energies for Mbyne and prenal formations deduced from the slope of the curves are 24.7 and 22.1 kJ mol^{-1}, respectively, these values are very close and this point will be discussed in Section 4.
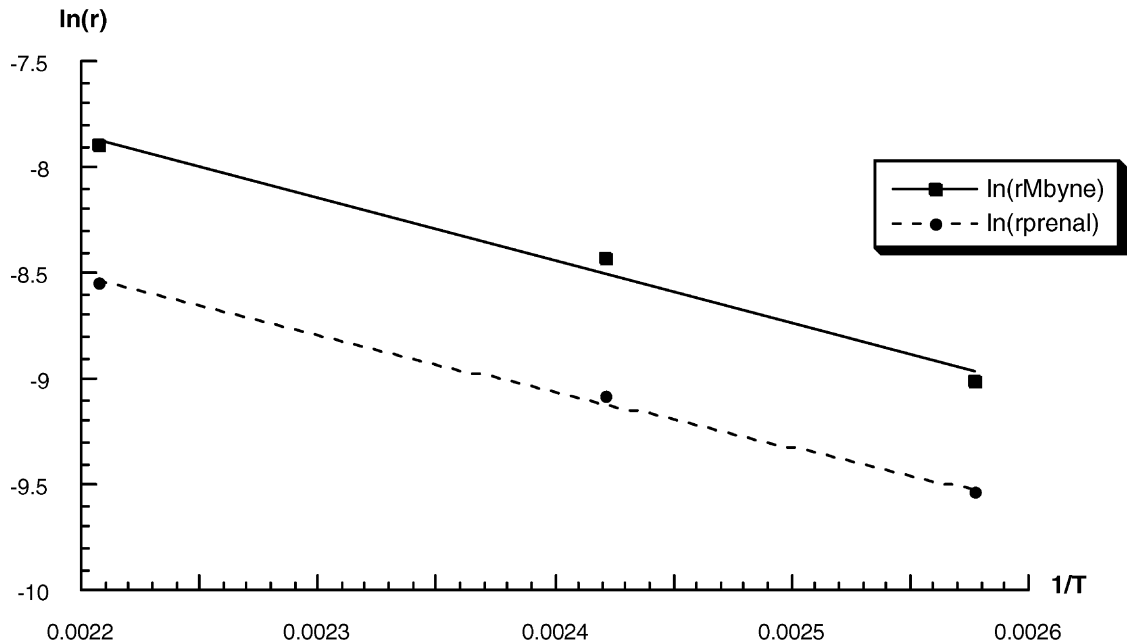

Fig. 6. Arrhenius plot for both reactions obtained on W_2N in standard conditions.

4. Discussion

From the kinetic data obtained, we deduced that MBOH produces Mbyne and prenal by two parallel reactions each one being zero-order. Their rates have been respectively, noted r_1 and r_2. Moreover, it has been seen that deactivation of the catalysts modified the conversion of MBOH but never the selectivities in Mbyne and prenal: the ratio r_1/r_2 is constant with time on stream. As deactivation occurs by poisoning active sites, we can infer that the same sites are implied in the formations of Mbyne and prenal. It is well known in literature, that MBOH undergoes dehydration to yield 2-methylbut-1-en-3-yne (Mbyne) on acidic catalysts [9,10,27]. Furthermore, oxo species of molybdenum, tungsten or vanadium have been claimed in homogeneous catalysis for the rearrangement of α-acetylenic alcohols into α,β-ethylenic carbonyl products [28]. More recently, data have been reported for the selective conversion of MBOH to prenal in the vapour phase [29] over MoO_3/SiO_2. Mechanistic explanations pointed out the necessity of oxo metallic species of molybdenum to allow the isomerization of MBOH to prenal.

We can thus propose that Mbyne and prenal formation takes place on the same type of site HO–M=O (with M = W, Mo or Nb). These reactions can be described by the two coupled catalytic networks (cycles 1 and 2) reported in Fig. 7. The first common elementary step corresponds to the adsorption of MBOH. It needs the hydroxyl group (Brönsted acidity) to eliminate a mole of H_2O and create the common intermediate (I). Then the cycle 1 leads to the Mbyne and the cycle 2 leads to the prenal by a concerted mechanism implying metalloxo intermediates leading to surface alkoxy intermediate. To be consistent with the zero-order reactions observed, the adsorption sites must be saturated. We have also shown that both reactions have similar activation energy. In fact the rate of each cycle can also be written using the kinetics parameters of the first common step:

$$r_1 = k_a [L_1] P_{MBOH} \text{ et } r_2 = k_a [L_2] P_{MBOH}$$

where k_a is the rate constant of adsorption of MBOH, $[L_1]$ and $[L_2]$ being the number of the same kind of sites respectively involved in cycle 1 and cycle 2: $[L] = [L_1] + [L_2]$, $[L]$ being the total site density.

As $[L_1]$ and $[L_2]$ are determined by entropic considerations [30], they do not depend on reaction temperature. So the apparent activation energy of each reaction is similar and directly linked to k_a.
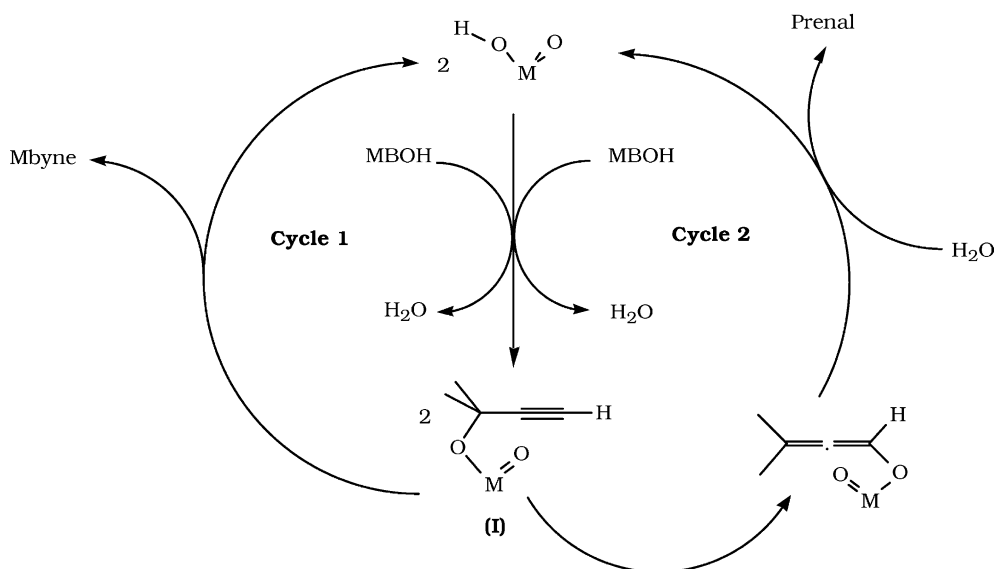

Fig. 7. Proposed mechanistic scheme.

Therefore, the second steps govern the relative rate of the two cycles [31]. The selectivity of the reaction directly depends on the ability of the metalloxo oxygen to give a nucleophilic attack on the acetylenic carbon atom and on the stability of the intermediate (I), which can be considered as a carbocation more or less stabilised by a basic oxygen, towards a proton elimination. The more the metallic centre atom will impose an acidic character, the more the nucleophilic attack will be difficult and the less the intermediate (I) will be stabilised by a poorly basic oxygen. The activity toward Mbyne will then increase with the acidic character of the metallic centre, while the activity toward prenal will be linked to the metalloxo species.

Oxo derivates of tungsten, molybdenum and niobium have already been characterised in heterogeneous catalysis by Raman spectroscopy [32]. Bernholc et al. have compared the Brönsted acid strength of some transition metal oxide clusters of titanium, niobium and tungsten by a theoretical method and have demonstrated that the number of terminal oxygen atoms forming a double bond with the transition metal atom has a strong effect on the Brönsted acidity. They have also found that the Brönsted acidity of unsupported clusters would follow the trend $TiO_x \ll NbO_x \ll WO_x$, as the valence requirements of the central metal result in 0, 1 and 2 double bonded terminal oxygen atoms. Moreover, concerning molybdenum, species with 2 double bonded terminal oxygen atoms have already been mentioned in the literature [33].

These results are in agreement with our catalytic data: even if the selectivity of NbN toward Mbyne is high, its activity toward Mbyne is less than the one of W_2N and Mo_2N. Moreover, its activity toward prenal is low because of the lack of metalloxo species as expected from previous results.

5. Conclusion

Reactions of MBOH (dehydration and isomerisation) over some transition metal nitrides clearly evidenced the acidic properties of these materials. Kinetic data permitted us to propose a mechanistic pathway involving a common step of adsorption for both reaction routes (kinetic coupling). A bifunctionnal site for adsorption was assumed: "M(=O)(OH)", possessing both Lewis and Brönsted acidities. The reaction rates r_1 and r_2 of MBOH dehydration to Mbyne and MBOH isomerisation toward prenal, are governed by the nature of the transition metal atom and its overall Lewis acidity. As $r_1/r_2 = [Mbyne]/[prenal] = [L_1]/[L_2]$ is known, counting of Brönsted acid sites should be conducted by complementary methods to evaluate both k_1 and k_2 separately.

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