Reduction of carbon monoxide by molybdenum-containing hydroxide systems

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The reduction of CO by the nitrogen-fixing systems $Ti(OH)_3$—$Mo(OH)_3$ and $MgTi_2O_4$—$Mo(OH)_3$ was studied in aqueous and water-methanol media; in the latter, ^{14}CO was used as the reagent. The main reaction product is methanol, whose yield in the H_2O—MeOH—KOH mixture is almost an order of magnitude higher than that in an aqueous alkaline solution. The data obtained were compared to those for the reduction of N_2.

Key words: Mo-hydroxide systems, carbon monoxide, reduction, methanol.

One of the specific features of systems reducing nitrogen in protic media is their ability (as well as that of nitrogenase[1]) to reduce acetylene, HC≡N, and N_3^- anions. Carbon monoxide, which is a strong inhibitor of reduction of N_2 in the case of both nitrogenase[1] and model systems,[2] is worthy of special consideration. The reduction of CO in the vanadium(II)—pyrocatechol system[3] has been previously studied in detail. In this work, we studied the reduction of CO by Mo^{III} hydroxide and the $MgTi_2O_4$—$Mo(OH)_3$ systems.

Experimental

The reduction of CO by the $Ti(OH)_3$—$Mo(OH)_3$ and $MgTi_2O_4$—$Mo(OH)_3$ systems was performed in an aqueous medium in an autoclave using the procedure developed for the reduction of N_2.[4,5] Experiments with ^{14}CO were carried out in a water-methanol alkaline medium in a Rittenberg vessel at atmospheric pressure.[3]

Gas chromatographic analysis of reaction products was performed on an LKhM-8MD chromatograph (flame-ionization detector, Porapak Q as the stationary phase, temperature of the column 90 °C, velocity of the carrier gas 50 mL min^{-1}, and volume of the sample 0.2 mL).

Radioactivity of solutions of reagents and reaction products was determined on an SL-30 scintillation spectrometer by the procedure described previously.[3]

Results and Discussion

Our experiments showed that, as in the V^{II}—pyrocatechol system,[3] methanol formed in the reaction

$$CO + 4\ Ti^{3+} \xrightarrow{Mo_2^{III}} MeOH + 4\ Ti^{4+}.$$

is the main reaction product.

A small quantity of methane (≤0.3% calculated per Mo) is formed along with methanol, which confirms the data of the work published previously.[6] In the absence of Mo^{III}, carbon monoxide is not reduced by Ti^{III} hydroxide, whereas individual $Mo(OH)_3$ reduces CO to form only methanol in amounts an order of magnitude lower than those in the case of mixed Ti—Mo hydroxide.

The study of the kinetics of accumulation of methanol in the aqueous molybdenum-containing systems (Fig. 1) shows that, in both cases, the rates of formation of methanol are approximately equal and comprise $v = 5 \cdot 10^{-7}$ mol $(L\ s)^{-1}$ at 55 °C.

As the temperature increases (Table 1), the yield of methanol in the MgTi—Mo system increases continuously, whereas in the Ti—Mo system the yield of MeOH passes through a maximum at 67 °C. This behavior of the systems correlates with the temperature dependence of their nitrogen-fixing activity.[7]

In the MgTi—Mo system, the yield of methanol reaches the limiting value already at $p_{CO} > 16$ atm

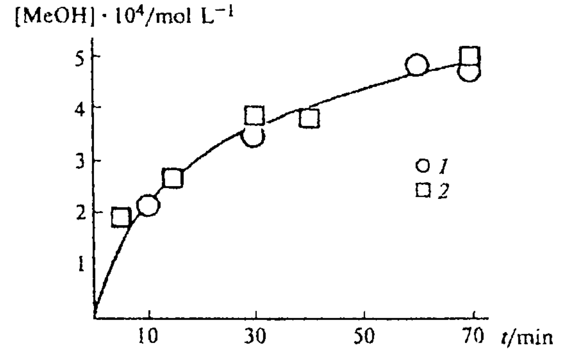

Fig. 1. Kinetics of formation of methanol during reduction of CO in $Ti(OH)_3$—$Mo(OH)_3$ (*1*) and $MgTi_2O_4$—$Mo(OH)_3$ (*2*) systems; [Mo] = $5 \cdot 10^{-3}$ mol L^{-1}, p_{CO} = 16 atm, 328 K, pH 14.2, reaction time 30 min.

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Table 1. Formation of methanol at different temperatures in aqueous alkaline $Ti(OH)_3$—$Mo(OH)_3$ and $MgTi_2O_4$—$Mo(OH)_3$ systems

T/K	[MeOH] · 10^4/mol L^{-1}	
	Ti—Mo	$MgTi_2O_4$—Mo
298	1.6	1.8
313	3.2	3.0
328	3.4	3.2
348	2.6	3.7
370	2.4	4.0

Note. Ti, $6 \cdot 10^{-4}$ mol L^{-1}; Mg : Ti = 0.5; Ti : Mo = 10; p_{CO} = 16 atm; *V* = 5 mL, reaction time 30 min.

(Fig. 2). It is noteworthy that in the case of nitrogen reduction even at p_{N_2} = 150 atm, no limitation of the yield of reaction products has been observed.[8]

The experimental data presented concern systems that function in aqueous media where their nitrogen-fixing activity is 8—10-fold lower than that in the water-methanol medium.[9] The use of methanol as the solvent does not allow one to determine its content in the reaction products of the CO reduction. Therefore, labeled ^{14}CO was used in experiments in water-methanol media (Table 2).

It is of interest that ~4% CO (calculated per Mo) is reduced to Mo^{III} hydroxide, and no methane is observed. As a whole, the experimental data obtained indicate that carbon monoxide is more reactive than N_2 and is reduced under milder conditions, despite the fact that the stability of the CO bond is 125 kJ mol^{-1} higher than the stability of the N≡N bond. For example, Mo^{III} hydroxide does not react with N_2, and in the $MgTi_2O_4$—$Mo(OH)_3$ system, dinitrogen is efficiently reduced only at $T > 350$ K.[7]

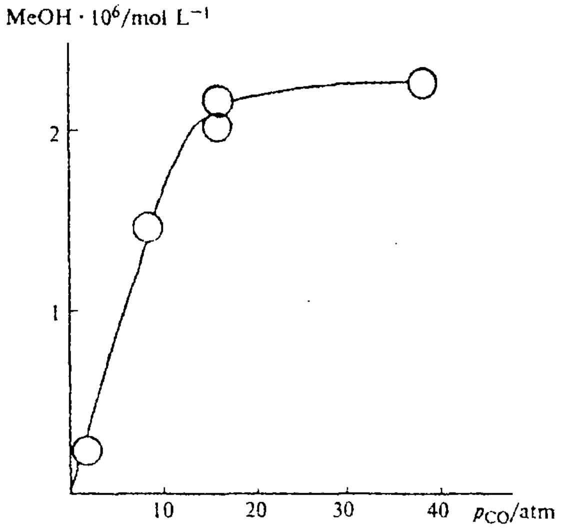

Fig. 2. Effect of p_{CO} on the yield of methanol during its reduction in the $MgTi_2O_4$—$Mo(OH)_3$ system (Mo, $2.5 \cdot 10^{-5}$ mol L^{-1}, 370 K, reaction time 30 min).

Table 2. Composition of products of reduction of CO by Mo^{III} hydroxides and $MgTi_2O_4$—$Mo(OH)_3$

System	CO	Yield of CH_4		Yield of MeMeOH	
		10^6/mol L^{-1}	%	10^6/mol L^{-1}	%
$MgTi_2O_4$—$Mo(OH)_3$	^{14}CO	1.60	1.45	11.1	37
	^{12}CO	0.76	0.69	Not measured	
$Mo(OH)_3$	^{14}CO	0		1.2	4
	^{12}CO	0		Not measured	

Note. Mg : Ti = 0.5; Ti : Mo = 10; Mo, $6 \cdot 10^{-5}$ mol L^{-1}; [KOH] = 1 mol L^{-1}, p_{CO} = 1 atm; MeOH—H_2O (5 vol.%), *V* = 10 mL, reaction time 30 min.

On the other hand, the reactions of reduction of CO and N_2 are similar under the conditions studied. For example, a decrease in the concentration of KOH results in a decrease in the yield of MeOH, and in a water-methanol system (see Table 2), the activity of the system increases by almost an order of magnitude, as for the reduction of N_2 to N_2H_4.[9] The sufficiently high yield of methanol (37% per Mo_2) at the atmospheric pressure of ^{14}CO with account for the data presented in Fig. 2 suggests a catalytic regime of the reaction at p_{CO} > 3—5 atm as occurs in the reduction of N_2. These specific features suggest, by analogy with the reduction of N_2, that hydride intermediates, hydroxo clusters of molybdenum formed under these conditions, participate in the CO reduction.[10]

It is noteworthy that in both the presence and absence of CO (for example, in an argon atmosphere), 3% formaldehyde calculated per Mo_2^{III} was observed in the reaction products. This also favors the assumption about the formation of the Mo—H bond, because it is known that in alkaline alcoholic solutions, some transition metals form compounds of CO with the metal—hydrogen bond,[11] and alcohols are oxidized to aldehydes.

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Reactions of terminal acylacetylenes with thiocarbohydrazones

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The reactions of terminal acylacetylenes with thiocarbohydrazones give 2-(2-acylvinyl)thiocarbohydrazones or 2,2-bis(2-acylvinyl)thiocarbohydrazones depending on the reagent ratio. Benzoylacetylene reacts with thiocarbohydrazone of *p*-dimethylaminobenzaldehyde to form *S*-[2-(*p*-dimethylaminobenzoyl)vinyl]isothiocarbodihydrazone.

Key words: acylacetylenes, 2-(2-acylvinyl)thiocarbohydrazones, 2,2-bis(2-acylvinyl)thiocarbohydrazones, *S*-(2-benzoylvinyl)isothiocarbodihydrazone, nucleophilic addition.

Previously, we have found that reactions of terminal acylacetylenes with thiosemicarbazones in a medium of acetonitrile, benzene, or methanol at 20 °C afforded 3-acylvinyl-5-amino-Δ^4-1,3,4-thiadiazolines in high yields.[1] The reactions of terminal acylacetylenes with thiocarbohydrazide in aqueous-ethanolic solutions at 60 °C gave 6-acylmethylhexahydro-1,2,4,5-tetrazine-3-thiones.[2]

As part of our continuing studies of the reactions of acylacetylenes with ambident nucleophilic *N*,*S*-containing reagents,[3—5] in this work we studied the reactions of ketones **1a,b** with thiocarbohydrazones **2a,b** and thiocarbodihydrazone **3**.

The reactions of acylacetylenes **1a,b** with thiocarbohydrazones **2a,b** in MeOH or MeCN at 20 °C gave the corresponding 2-(2-acylvinyl)thiocarbohydrazones (**4a—c**) as the only products (Scheme 1). We did not observe the formation of adducts as a result of attack at the triple bond of acetylenes **1a,b** with the participation of the *S*-nucleophilic center of reagents **2a,b**. Evidently, the *S*-nucleophilic center is less nucleophilic than the NH_2 group of hydrazones **2a,b**, whose high nucleophilicity is attributable to the α-effect and to interactions of the lone electron pair of the nitrogen atom of the NH_2 group with the orbitals of the lone electron pair of the adjacent nitrogen atom.[6—8]

The reactions of thiocarbohydrazones **2a,b** with an excess of acetylene-containing ketones **1a,b** gave *N*-diadducts **5a,b** in good yields.

The reaction of ketone **1a** with thiocarbodihydrazone **3**, which does not contain the primary amino group, proceeded differently. In **3**, the S atom serves as the nucleophilic center, which leads to the formation of *S*-monoadduct **6**.

The IR spectra of compounds **4a—c**, **5a,b**, and **6** have absorption bands of the C=O bonds (1615—1640 cm^{-1}), of the C=N and C=C bonds (1515—1605 cm^{-1}), and of the NH stretching vibrations (3120—3230 cm^{-1}). In addition, the spectra of compounds **4a—c** and **5a,b** have absorption bands of the C=S bonds (1200—1210 cm^{-1}) and the spectrum of **6** has an absorption band of the C—S bond (690 cm^{-1}).

Experimental

The ^1H NMR spectra (in DMSO-d_6) were obtained on a BS-487C spectrometer operating at 80 MHz. The IR spectra were recorded on a Specord IR-75 instrument as KBr pellets.

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