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The effect of Mo on the catalytic and surface properties of Rh–Mo/ZrO_2 catalysts

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A series of Rh–Mo/ZrO_2 catalysts with fixed Rh and different Mo loadings were prepared and characterized by H_2 chemisorption, XRD, TPR, TEM and XPS. The catalysts were studied in two reactions: the hydrogenation of carbon monoxide and the hydrogenation of toluene. The results suggest that the increase in the Mo content produces a partial coverage of the support and the Rh particles. Moreover, at high Mo coverage, an increase of the MoO_3 layer thickness is produced. After being treated in hydrogen, the molybdenum oxide remains as slightly reduced particles, while Rh is essentially as Rh^0, with only a small contribution of Rh^+ species. The Mo promotes the formation of oxygenates in the CO hydrogenation and it does not affect the activity in the hydrogenation of toluene.

Keywords: rhodium; molybdenum; chemisorption; TPR; XPS; hydrogenation

1. Introduction

Among the many CO hydrogenation catalysts, Rh is known as a catalyst for producing oxygenated compounds [1–7]. The chemical state of rhodium affects strongly the conversion and the resulting hydrogenation products. When rhodium is in the metallic state only oxygen free hydrocarbons are obtained [8]. However, if rhodium is partially oxidized, i.e. Rh^+, the selectivity to methanol is strongly enhanced [9]. The nature of the support, metal precursor, metal particle size and promoters can affect the electronic state of supported rhodium catalysts and also the selectivity for the hydrogenation of carbon monoxide [8,9–12].

The effect of the carrier has been widely studied [8,13–16]. SiO_2, TiO_2, Al_2O_3, MgO, La_2O_3, ZnO and ZrO_2, among others, have been used as a support of Rh for CO hydrogenation. Even the mechanism of the influence of the carrier on chemisorptive and kinetic parameters is still under discussion; it seems that the support with intermediate acidity is more appropriate for obtaining oxygenated compounds from synthesis gas.

The influence of promoters may be associated with an electronic effect involving charge transfer from the promoter to the metal or producing the blockage of surface sites or changing the reaction intermediates by interaction between the promoters with reactant molecules [17–21].

One of the interesting promoters is Mo. Important changes in product distribution and activity have been reported when Mo is added to Rh/SiO_2 catalysts [12,22,23].

In this work, we study the effect of Mo loading on a series of Rh–Mo/ZrO_2 catalysts in the hydrogenation of carbon monoxide and in the hydrogenation of toluene. The catalysts were characterized by the evaluation of specific surface area, H_2 chemisorption, temperature programmed reduction, X-ray diffraction, transmission electron microscopy and X-ray photoelectron spectroscopy. The characterization results are correlated to activity results.

2. Experimental

ZrO_2 used as carrier of the catalysts was prepared by precipitation at room temperature of zirconium oxychloride solution with an excess of ammonia solution. The solid obtained was filtered, washed with distilled water until the chlorine was removed. Then it was dried at 393 K overnight and calcined in air at 823 K for 2 h.

Rh–Mo supported catalysts containing 2 wt% Rh and variable amount of Mo ranging from 1 to 10 wt%, were prepared by impregnation of the support with an aqueous solution of ammonium heptamolybdate (Merck). After impregnation, the samples were dried overnight in air at 393 K and then calcined in air at 673 K.

Then the samples were impregnated with an aqueous solution of rhodium trichloride (Aldrich). After impregnation, the samples were dried at 393 K and then calcined in air at 573 K. The solids were reduced in situ before the characterization or the catalytic test. In each case the catalysts were reduced in situ in flowing H_2 (50 cm^3/min) at 573 K for 30 min at atmospheric pressure.

The adsorption measurements were carried out in a greaseless volumetric system. The specific surface area was evaluated by nitrogen adsorption at 77 K and H_2 uptake from hydrogen adsorption isotherm at 298 K. The method of Benson and Boudart [24] and Wilson and Hall [25], in which the linear portion of the isotherm determined between 50 and 250 Torr is extrapolated to zero pressure, has been used to determine the hydrogen uptake.

TPR experiments were carried out in a conventional system using a 5% H_2/Ar (40 $cm^3\ min^{-1}$) mixture and a heating rate of 8 K min^{-1}. H_2 consumption was monitored by a system having catherometric detection. XRD patterns were obtained using a Rigaku powder diffractometer using nickel filtered Cu Kα radiation. TEM studies were carried out in a Jeol model JEM-1200 EX II system.

XPS spectra were obtained using a Fisons Escalab 200R spectrometer with a hemispherical analyzer operated in the constant pass energy mode. Unmonochromatized Mg Kα X-ray radiation ($h\nu = 1253.6$ eV) operated at 10 mA an 12 kV was used as exciting source. The spectrometer was equipped with a high pressure reaction cell to carry out pretreatments at high temperatures. The samples were pressed in a hydraulic die to form thin smooth discs and placed in the high pressure cell. Afterwards, the samples were reduced in H_2 at 573 K for 30 min. Then they were transported to the analysis chamber without contact with air. The C 1s line at a binding energy of 284.9 eV was used as an internal standard. The intensity of various XPS peaks was determined using s-shaped background subtraction and integration of peak areas. Rhodium and molybdenum peaks were deconvoluted into several components assuming that the peaks had Gaussian–Lorentzian shapes. The Rh/Zr and Mo/Zr ratios were estimated from the integrated intensities of Rh 3d, Mo 3d and Zr 3d, using the sensitivity factors from Wagner et al. [26].

The hydrogenation of CO was investigated in a stainless steel (coated with gold) reactor at 533 K and 15 atm. The catalysts were reduced in situ at 573 K in flowing hydrogen at atmospheric pressure. Then the reactor was cooled to the reaction temperature and a mixture $H_2 : CO = 3 : 1$ at 15 atm was fed into the reactor. The reactants and products were analyzed by an on-line Gow-Mac gas chromatograph. Steady state activity and product distribution were achieved after 90 min of reaction.

Toluene hydrogenation was studied in a fixed-bed microcatalytic reactor working at atmospheric pressure. For this reaction a flow of 30 $cm^3\ min^{-1}$ of a H_2/toluene = 112 (molar ratio) mixture was fed into the reactor. The reaction temperature ranged between 313 and 358 K. Only 25 mg catalyst samples were used so as to keep low conversion levels and to avoid mass and heat transfer limitation. The analyses were carried out by an on-line Gow-Mac gas chromatograph.

3. Results and discussion

Table 1 compiles specific surface areas and H/Rh atomic ratios derived from hydrogen chemisorption measurements at 298 K.

From the data in table 1 it is clear that surface areas do not change significantly upon increasing molybdenum loading. However, the H/Rh ratios drop drastically with increasing molybdenum loading. A similar trend was reported recently for Rh–Mo/SiO_2 catalysts [23]. Storm et al. [27] and Shen et al. [23] also reported the decrease in hydrogen uptake when Mo is present in Rh supported catalysts. This behaviour cannot be attributed to a decrease in metal dispersion, because XRD showed only the diffraction lines due to the support. No lines due to Rh or MoO_3 particles were detected indicating a high dispersion of these phases. In addition,

Table 1
Specific surface areas and H/Rh atomic ratios for Rh–Mo/ZrO$_2$ catalysts

Catalyst	S_{BET} (m^2 g^{-1})	H/Rh
Rh(2)Mo(1)	55.1	0.27
Rh(2)Mo(2)	55.4	0.19
Rh(2)Mo(3)	58.5	0.12
Rh(2)Mo(5)	56.4	0.10
Rh(2)Mo(7)	51.8	0.05
Rh(2)Mo(10)	67.2	0.025

TEM results showed similar particle size distribution for all the studied catalysts with an average particle size of 5.0 nm (fig. 1). Therefore the decrease in the H/Rh ratio may be attributed to a coverage of the Rh particles with highly dispersed MoO$_3$.

A TEM micrograph of the Rh–Mo/ZrO$_2$ catalyst is displayed in fig. 1. Particle size analysis indicates a rather narrow size distribution, with particles ranging between 4 and 6 nm. Similar patterns were found for all the catalysts. According to these data, the strong inhibition in hydrogen chemisorption in reduced catalyst cannot be explained in terms of a decrease in the Rh dispersion. It seems that molybdenum oxide covers a fraction of the metal particles and a larger coverage of Rh crystallites occurs with increasing molybdenum content.

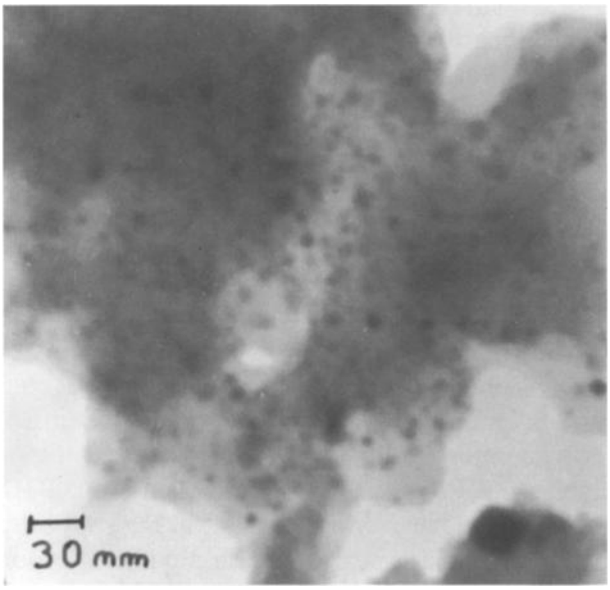

Fig. 1. TEM micrograph. Catalyst: Rh(2)Mo(3)/ZeO$_2$.

TPR profiles in the temperature range 293–823 K for the calcined samples are displayed in fig. 2. In all cases a single peak at around 368 K can be discerned. As occurs for the parent Rh/ZrO$_2$ catalyst, which shows a single TPR peak at ca. 368–393 K, such a peak can be ascribed to the reduction of rhodium oxide to metallic Rh. The reduction of molybdenum oxide takes place at higher temperatures. Thus, while the reduction of bulk MoO$_3$ begins at temperatures above 893 K, for silica-supported molybdenum oxide such a process starts at 753 K [28]. In the present work, the observation of a new reduction peak above 773 K is consistent with the reduction of crystalline MoO$_3$. For the catalysts with Mo-loading below 3%, the extent of the reduction of oxidic rhodium species as measured by H$_2$ consumption is somewhat below the expected value from the Rh$_2$O$_3$ stoichiometry. This result suggests a strong Mo–O–Rh interaction, which makes the complete reduction of catalysts difficult [29–31]. For the Rh(2)Mo(3)/ZrO$_2$ catalyst, hydrogen consumption resulted close to the stoichiometric value for a complete reduction of Rh^{3+} into Rh, and for higher Mo contents this exceeded the stoichiometric amount. This is in line with the expectations for a partial reduction of the MoO$_3$ phase at high temperatures, which is confirmed by photoelectron spectroscopy. At temperatures higher than 850 K a reduction of bulk MoO$_3$ takes place.

The Rh 3d and Mo 3d core level spectra of catalysts reduced at 573 K are shown in figs. 3A, 3B and 3C, respectively. The BE of the Rh 3d$_{5/2}$ peak at ca. 307.2 eV

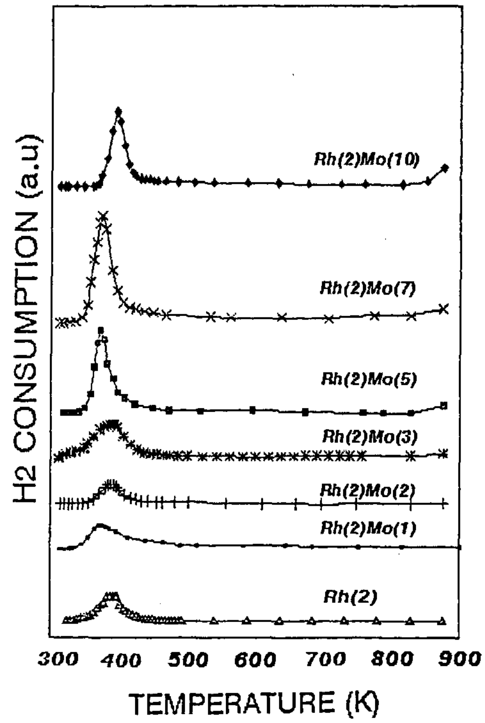

Fig. 2. Temperature programmed reduction profiles of various Rh–Mo/ZrO$_2$ catalysts.

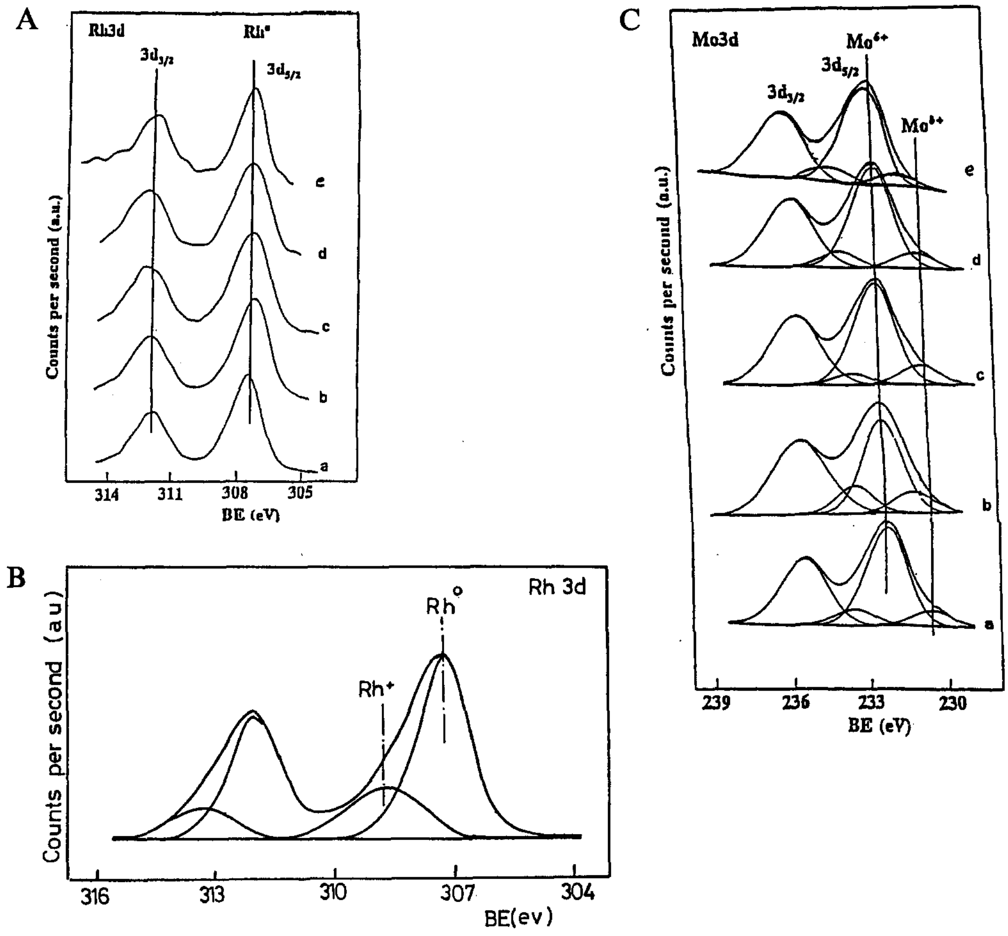

Fig. 3. XP spectra for (A) Rh and (C) Mo 3d core level of different Rh–Mo/ZrO_2 catalysts prereduced in H_2 at 573 K. (B) Rh 3d core level of Rh(2)Mo(2)/ZO_2 catalysts pretreated in a mixture $H_2 : CO = 1 : 1$ at 473 K.

for catalysts containing 1–3% Mo shifts slightly (ca. 0.3 eV) towards higher BE values for the parent catalysts containing higher Mo-loadings. Even considering the accuracy in BE measurements, which is in the order of 0.1 eV, and that Rh and Rh^+ have BEs of 307.2 eV and 307.6–309.6 eV [8], respectively, Rh seems to be the major rhodium species although a certain proportion of Rh^+ species can be present in the catalysts with higher Mo-loadings. In order to investigate the nature of surface Rh species present under reaction conditions, a representative Rh(2)Mo(2)/ZrO_2 catalyst has been prereduced at 473 K within the pretreatment chamber of the spectrometer and then exposed to a $H_2 : CO = 1 : 1$ mixture, 0.60 bar total pressure at 523 K for 1 h, which simulates CO hydrogenation conditions. The Rh 3d profile displayed in fig. 3B shows clearly the presence of both Rh^0 (65% of the total peak area) and Rh^+ (35% of the total peak area). This experiment nicely illustrates the stabilization of Rh$^+$ species under CO + H$_2$ mixture. This behaviour clearly contrasts with the observation of completely reduced Rh species when exposed to a H$_2$ atmosphere under similar temperature. The Mo 3d profiles for catalysts with Mo contents up to 3 wt% (fig. 3C) display symmetric Mo 3d peaks, however these profiles are rather asymmetric and more complex for higher Mo contents. For catalysts with Mo contents between 5 and 10% curve fitting procedures of the experimental spectra show partially reduced molybdenum species in a proportion below 20%. This result, which is in good agreement with TPR experiments, indicates that metallic Rh catalyzes the reduction of MoO$_3$ catalysts with higher Mo content.

Quantitative XPS data are compiled in table 2. It can be seen that the Mo/Zr surface ratios reach almost constant values at Mo-loadings close to 5 wt%. By assuming a value of 0.20 nm^2 for the area covered by each MoO$_3$ entity, the Mo-loading required for a complete coverage (57 m^2/g) of the carrier surface is 4.5 wt% MoO$_3$. The good accordance between experimental result and calculations for monolayer dispersions indicates that MoO$_3$ is very well dispersed up to loadings close to 5 wt%. On the other hand, Rh/Zr ratios increase with Mo-loadings reaching a maximum value at ca. 3 wt% and then decrease at higher contents. This behaviour can be understood in terms of a gradual coverage of both zirconia and Rh surfaces. Thus, even the exposed Rh atoms decrease with increasing Mo-loading, the decrease of surface Zr atoms is still more marked and therefore the Rh/Zr ratio increases. At higher Mo-loading the coverage by MoO$_3$ is higher and most of the Rh particles remain under the MoO$_3$ layer leading to a reduction of the Rh/Zr ratio.

Activity data for CO hydrogenation at 533 K, 15 bar overall pressure and H$_2$: CO = 3 : 1 molar ratio for the representative Rh(2)Mo(7)/ZrO$_2$ catalyst are displayed in fig. 4. This figure represents stationary state data which were reached after 5 h on-stream. Similar plots were found for the other catalysts although conversion levels and methanol selectivities varied from catalyst to catalyst. Selectivity to methanol as a function of the MoO$_3$ loading is shown in fig. 5. At low MoO$_3$ content the selectivity to methanol is rather low, hydrocarbons being the major reaction products. However, at high MoO$_3$ contents the selectivity to methanol is rather high reaching an almost constant value around 40%.

Table 2
Rh/Zr and Mo/Zr surface atomic ratios in Rh–Mo/ZrO$_2$ catalysts

Catalyst	Rh/Zr	Mo/Zr
Rh(2)Mo(1)	0.0030	0.0371
Rh(2)Mo(2)	0.0094	0.0842
Rh(2)Mo(3)	0.0180	0.0785
Rh(2)Mo(5)	0.0113	0.1333
Rh(2)Mo(7)	0.0095	0.1472
Rh(2)Mo(10)	0.0083	0.1746

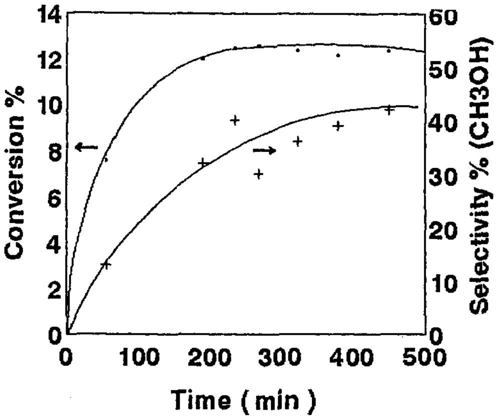

Fig. 4. CO conversion and selectivity to methanol at 533 K and 15 atm. Catalyst: Rh(2)Mo(7)/ZrO$_2$.

In fig. 6 the catalytic activity expressed as turnover number referred to the total conversion (TONa) and the conversion to methanol (TONb) is given. The same trends for both curves can be observed. They increase drastically when the Mo content increases, reaching comparable values at higher Mo loading. This behaviour may be explained considering that at low Mo content, Mo is present as MoO_3 and Rh as Rh crystals. Increasing the Mo content, the surface coverage of the support increases making an intimate contact of MoO_3 with Rh particles, present mainly as Rh, the molybdenum oxide being slightly reduced. This $Rh–Rh^+–MoO_{3-x}$ catalyst may be suggested as the active site for this system. A similar enhancement in the rate of hydrogenation of CO over MoO_3-promoted Rh catalysts has been previously reported [32,33].

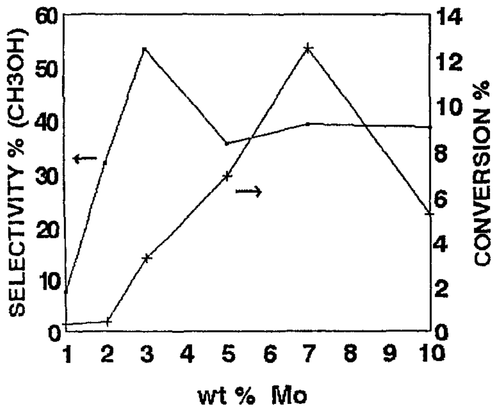

Fig. 5. Relation of Mo content with conversion and selectivity to methanol in Rh(2)Mo(x)/ZrO$_2$ catalysts. $T = 533$ K; $P = 15$ atm.

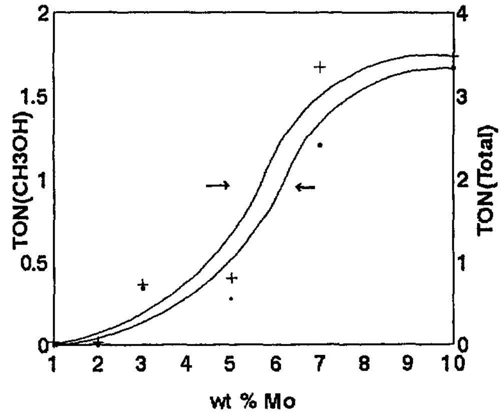

Fig. 6. Turnover number for total conversion (TONa) and conversion to methanol (TONb) for Rh(2)Mo(x)/ZrO_2 catalysts. TON in molec./s x at. Rhs.

Toluene hydrogenation was also used as test reaction for the same catalyst series. In all cases, methylcyclohexane was the only reaction product. Although this reaction was less studied than benzene hydrogenation, it is a useful reaction test for metal catalysts characterization [23]. Table 3 compiles TON values for two different reaction temperatures and activation energies for this reaction. As expected, activity increased with temperature and for a given temperature this remained essentially constant irrespective of Mo-loading. This finding suggests that metallic Rh is the active site for hydrogenation with no inhibition by the presence of MoO_3. With regard to the activation energies, these values are in good agreement with those reported previously for Pt catalysts for the same reaction [34,35], even considering that reported TON values for the same reaction at 333 K are one order of magnitude higher for Pt catalysts [36,37].

Table 3
Turnover number for hydrogenation of toluene at 313 and 323 K and activation energies for Rh(2)Mo(x)/ZrO_2 catalysts

Catalyst	TON[a] (313 K)	TON[a] (333 K)	E (kcal/mol)
Rh(2)Mo(1)	6.8×10^{-3}	1.76×10^{-2}	9.9
Rh(2)Mo(2)	6.2×10^{-3}	1.80×10^{-2}	11.4
Rh(2)Mo(3)	6.8×10^{-3}	1.83×10^{-2}	10.3
Rh(2)Mo(5)	6.4×10^{-3}	1.70×10^{-2}	10.2
Rh(2)Mo(7)	5.8×10^{-3}	1.57×10^{-2}	10.4
Rh(2)Mo(10)	6.1×10^{-3}	1.90×10^{-2}	10.2

[a] TON is expressed as number of molecules converted at Rhs. To evaluate the number of Rh surface atoms a stoichiometry of adsorption Rhs : H = 1 : 1 was used.

4. Conclusions

Mo promotes the formation of methanol in the CO hydrogenation and it does not affect the activity per site in the hydrogenation of toluene.

MoO_3 does not only cover the surface of the support but also part of the rhodium particles, decreasing the H_2 uptake and producing a slight modification on the oxidation state of Rh. At the same time in the catalysts with higher Mo content, partially reduced MoO_{3-x} was produced.

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