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Modified W/HZSM-5 catalysts: structure and catalytic properties

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Abstract

Conventional aqueous impregnated W/HZSM-5 catalysts have been modified by treatment with an 1 M ammonia aqueous solution prior to the calcination step, obtaining tungsten loading in the range 0.02–0.2 wt.%. UV diffuse reflectance spectroscopy (UV DRS), X-ray diffraction (XRD), temperature-programmed reduction (TPR), temperature-programmed desorption of ammonia (TPDA), surface area measurement, scanning electron microscope (SEM) and TEM were used for the characterization of the samples. The catalysts obtained were almost exclusively constituted of monomeric tungsten species. The characterization findings let us draw a model in which these species are chemically joined to the Brønsted acid sites of the HZSM-5 zeolite and, therefore, well dispersed on the support. These catalysts were tested in the partial oxidation of methane to formaldehyde at atmospheric pressure. The obtained formaldehyde yields were up to three times higher than those of the conventional aqueous impregnated W/HZSM-5 catalysts. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: W/HZSM-5 catalyst; Supported tungsten species; Oxidation of methane (partial); Formaldehyde

1. Introduction

In the last years many papers have been focused on the study of the effect of the support on the properties and the catalytic behavior of metal oxides active in a given reaction. The support may not only increase the dispersion of the active phase but also facilitate the formation of surface species characterized by a high activity and a good selectivity [1].

MoO₃ and V₂O₅ supported catalysts are specially promising for selective oxidation reactions having showed an excellent behavior in the catalytic partial oxidation of methane to C₁ oxygenates [2,3]. Recent papers show that the catalytic properties of supported MoO₃ and V₂O₅ are strongly affected by the metal

oxide-support interaction, which controls both reducibility and dispersion of the active phase [4–7]. It has been reported that the activity of the catalyst in methane activation is affected by the catalyst reducibility. This parameter depends on several factors such as metal oxide loading and nature of the support [7,8]. On the other hand, the dispersion of the active phase determines the kind of metal oxide species formed on the support. The comprehension of the role of these supported species in the reaction mechanism is a key to increase the formaldehyde selectivity and, subsequently, the reaction yield. Several active sites have been described for silica-supported molybdena and vanadium oxide catalysts. It seems to be a general agreement in the catalytic role of each active site in the methane partial oxidation [3,9–12]. Thus, M=O sites (M = Mo, V) of terminal atoms in metal oxide crystallites or isolated monomeric species seem to be specific sites for HCOH production, while M–O–M

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sites of polymeric species and metal oxide cluster would lead to the total oxidation products.

Since W and Mo are closely related chemically, it is reasonable to expect these two catalysts to exhibit similar structural features. Based on this idea, we have reported several papers dealing with the characterization of supported WO_3 and MoO_3 catalysts prepared by conventional aqueous impregnation and their catalytic properties in the partial oxidation of methane to formaldehyde. HZSM-5 zeolite has been the main support used but precipitated silica has been also employed [12–15]. As expected, the obtained results showed a certain parallelism in the structure of the supported metal oxide phase for both W/HZSM-5 and Mo/HZSM-5 catalysts [15]. It was shown that the kind of metal oxide species formed on the catalyst was dependent on both metal oxide loading and the nature of the support surface [14]. Thus, monomeric species with $\text{M}=\text{O}$ sites, probably joined to the acid sites of the zeolite, were the responsible of the selective production of formaldehyde reaching STY values up to ca. $60 \text{ g kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ [12,15].

In this paper, the preparation of W/HZSM-5 catalysts mainly constituted of monomeric W species is reported. For this purpose, HZSM-5 zeolite was impregnated with ammonium metatungstate solution and then washed with ammonia aqueous solutions. The resulting catalysts were used in the partial oxidation of methane to formaldehyde and compared to those W/HZSM-5 samples without ammonia treatment [13].

2. Experimental

2.1. Catalyst preparation

NaZSM-5 zeolite ($\text{Si}/\text{Al} = 45$) was synthesized according to the method described elsewhere [16] using ethanol as template. X-ray diffraction (XRD) confirmed that the product was 100% crystalline. Fully exchanged HZSM-5 (checked by chemical analysis) was obtained by ion exchange of 10 g of the zeolite with 200 ml of 0.6 M aqueous solution of HCl followed by drying at 110°C overnight.

The first step of the preparation method was the aqueous impregnation of the HZSM-5 zeolite with solutions of ammonium metatungstate, according to an earlier procedure [13]. The HZSM-5

zeolite powder was contacted in a rotary evaporator with aqueous solutions of ammonium metatungstate, $(\text{NH}_4)_6\text{W}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ (10 ml of solution per g zeolite). The concentration of the salt was adequately selected in order to yield tungsten loading in the range 0.8–11.9 wt.%. After 4 h of stirring at ambient temperature, the water was completely removed by evaporation at 70°C under vacuum. These materials were further treated with an ammonia aqueous solution in order to remove the physically adsorbed tungsten species of the catalysts. 10 g of dry sample were stirred for 5 min with 200 ml of 1 M ammonia solution, then filtered and repeatedly washed with deionized water. Finally the samples were dried at 110°C for 4 h and calcined at 675°C for 2.5 h. The catalyst will be referred to as t-ZW x (treated W/HZSM-5 catalysts), x indicating the final tungsten loading of the catalyst.

2.2. Catalytic tests

The catalytic tests were carried out in a fixed bed continuous flow quartz reactor (internal diameter: 21.4 mm) at 650°C . A standard reactant mixture of methane and oxygen (5.3:1 molar ratio) without diluent was used at ambient pressure. The flow rates of both reactants were controlled by calibrated Brooks mass flow meters. Space velocity of the feed was $7.41 \text{ g h mol}^{-1}$. The reactor was heated by means of an oven with three independently controlled heating zones. A thermocouple was placed in the center of the bed in order to measure the reaction temperature (bed axial variation being only $\pm 5^\circ\text{C}$). The effluent streams were analyzed by a Hewlett–Packard 5890A gas chromatograph equipped with a TCD detector and two columns: a Porapak Q column to separate CH_4 , CO_2 , $\text{CO} + \text{O}_2$, HCOH and water and a molecular sieve 5A packed column to separate CO and O_2 . Calibration for formaldehyde was obtained with a 40% HCOH aqueous solution. In the present research, the carbon balance between methane consumed and HCOH , CO and CO_2 produced was always better than 97%.

Prior to the runs, catalyst samples were pretreated “in situ” in an oxygen flow from the ambient temperature to the reaction temperature, 650°C , and held at the latter about 1 h. Approximately 2 h were required to reach apparently steady state conditions. Sampling of the product stream was repeated until the analytical results were reproducible.

2.3. Catalyst characterization

Tungsten analyses were carried out in the Galbraith Laboratories (Knoxville, USA) by ICP-AES. BET surface area and micropore volume of the calcined samples were measured by using a Quantachrome Autosorb-1 apparatus with nitrogen as the adsorbate. X-ray powder diffraction patterns were recorded on a Philips PW1710 diffractometer using Cu K α radiation. Scanning electron microscope (SEM) micrographs were obtained with a Philips XL30-CPDX4i SEM on Au metallated samples. TEM images were recorded using a JEOL JEM-2000 FX transmission electron microscope operating at 200 kV. UV diffuse reflectance spectra (UV DRS) were performed by using Spectralon as a reference on a Perkin-Elmer Lambda-20 spectrometer equipped with a diffuse reflectance accessory. The spectra were recorded immediately after calcination of the samples. The scanning wavelength range was 198–500 nm and the scan speed was 120 nm min⁻¹. TPR experiments were recorded on a Micromeritics TPD/TPR analyzer. The samples were pretreated from ambient temperature to 675°C in argon flow. Following pretreatment, TPR experiments were run in a 17% H₂/Ar stream (50 N cm³ min⁻¹) heating up to 900°C at a rate of 10°C min⁻¹. During this time the exit gas was monitored using a TCD detector. Total acid site density of the catalysts was measured by a temperature-programmed desorption of ammonia (TPDA) by means of a Micromeritics TPD/TPR analyzer. The samples were housed in a quartz tubular reactor and pretreated in flowing helium while heating at 15°C min⁻¹ to 675°C. After a period of 30 min at 675°C, the samples were cooled at 180°C and saturated by flowing a pure ammonia stream for 15 min. The catalysts were then allowed

to equilibrate under helium flow at 180°C for 1 h. Finally, the ammonia was desorbed by using a linear heating rate of 15°C min⁻¹ up to 675°C. Temperature and detector signals were simultaneously recorded. The unique area under the curve was integrated to determine the total acidity of the catalyst.

3. Results and discussion

3.1. Catalyst characterization results

Tungsten loading and BET surface areas of the t-W/HZSM-5 catalysts are shown in Table 1. As seen, the treatment with NH₃(aq) brings about the removal of a significant amount of tungsten (from 0.8–11.9 to 0.02–0.20 wt.%), presumably the physisorbed species. In spite of the low tungsten contents obtained, surface area of the samples decreases meaningfully as tungsten loading increases. This indicates a strong interaction between zeolite surface and the tungsten species that enables a good dispersion [4]. This decrease is more pronounced for the samples with the highest W content, i.e. t-ZW 0.10 and t-ZW 0.20. This fact can be attributed to the partial blocking of the zeolite channels caused by the entrance or deposition of tungsten species. Similar conclusions have been reported for the untreated W/HZSM-5 catalysts [13] and for Mo/HZSM-5 catalysts [17,18].

TPR profiles of the catalysts and the bulk WO₃ are given in Fig. 1. The TPR pattern of bulk WO₃ exhibits two peaks with maxima at 655 and 740°C. These peaks may be assigned to the two step-wise reduction of WO₃ to W(0) (W(VI) → W(IV) → W(0)) [14]. TPR profiles of the samples do not show any hydrogen consumption in the range 300–900°C with except to

Table 1
Characterization parameters of the treated W/HZSM-5 catalysts

| Catalyst | Tungsten content (wt.%) | BET surface area (m ² g) | Relative total acidity ^a |
|-----------|-------------------------|-------------------------------------|-------------------------------------|
| HZSM-5 | 0 | 307 | 1.00 |
| t-ZW 0.02 | 0.02 | 279 | 0.93 |
| t-ZW 0.05 | 0.05 | 273 | 0.91 |
| t-ZW 0.06 | 0.06 | 269 | 0.92 |
| t-ZW 0.07 | 0.07 | 271 | 0.90 |
| t-ZW 0.10 | 0.10 | 260 | 0.92 |
| t-ZW 0.20 | 0.20 | 249 | 0.91 |

^a Calculated as (mmol NH₃ per g)_{cat}/(mmol NH₃ per g)_{HZSM-5}.

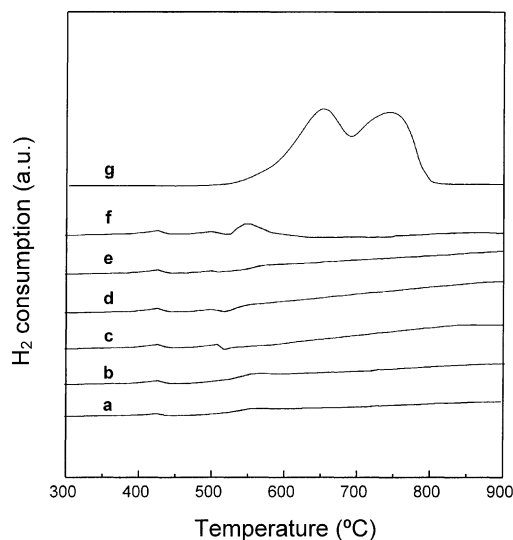


Fig. 1. Temperature-programmed reduction profiles of t-W/HZSM-5 catalysts: (a) t-ZW 0.02; (b) t-ZW 0.05; (c) t-ZW 0.06; (d) t-ZW 0.07; (e) t-ZW 0.10; (f) t-ZW 0.20; (g) bulk WO_3 .

the highest loaded catalyst. We have reported that the reducibility of this type of catalysts decreases as the strength of the interaction metal oxide species-support surface increases [12–14]. Similar findings have been reported by Faraldos et al. for $\text{MoO}_3/\text{SiO}_2$ catalysts [8]. The results shown in this paper point out the existence of tungsten species attached to the HZSM-5 zeolite and, therefore, well dispersed on the support surface. The existence of a single reduction peak for the t-ZW 0.20 sample may indicate the presence of partially reducible polymeric tungsten species in some extent.

The UV DRS of all the catalysts (Fig. 2) present a band at about 230–240 nm. This band is the unique for all the samples excepting for the t-ZW 0.10 and t-ZW 0.20 catalysts. These samples exhibit an additional band, as a shoulder, at about 265 nm. According to the reported wavelength for oxotungsten species [13,14], the band at 230–240 nm could be assigned to tetrahedrally coordinated W(VI) species while the band at about 265 nm could be assigned to octahedral polyoxotungstate W(VI) species. Therefore, the low loaded catalysts contain exclusively monomeric W species while the samples with the highest loading present low amounts of polyoxotungstate species. It

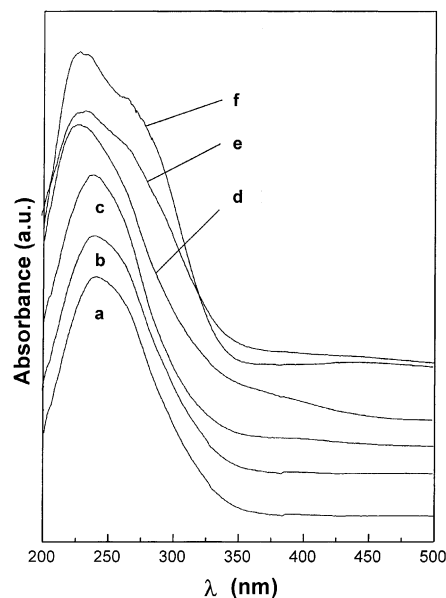


Fig. 2. UV diffuse reflectance spectra of t-W/HZSM-5 catalysts: (a) t-ZW 0.02; (b) t-ZW 0.05; (c) t-ZW 0.06; (d) t-ZW 0.07; (e) t-ZW 0.10; (f) t-ZW 0.20.

is reasonable to assume that both type of W species are chemically joined to the zeolite surface since they remain on the catalyst after the ammonium washing treatment. As expected, the XRD spectra and TEM micrographs of the samples confirmed the absence of a WO_3 crystalline phase. These results strongly confirm the TPR findings.

The relative acidity values of the catalysts, evaluated by TPD of ammonia, are shown in Table 1. It can be seen that the acidity of the tungsten samples decreased compared to the HZSM-5 zeolite. In spite of the different tungsten loading of the samples, the observed decrease is very similar for all of ones. This fact could indicate a good dispersion of the tungsten species in the low loaded samples, larger than in the higher loaded ones. This fact will be discussed in the next section.

3.2. Surface tungsten species

In a previous paper regarding to W/HZSM-5 catalysts [13], it was reported the presence of both polymeric and monomeric tungsten species in the samples after impregnation stage. The existence of

the former ones was expected having into account the pH-dependent behavior of the tungstate ion (the polytungstate anion is the predominant in acidic solutions while the tungstate ion is stable in neutral or alkaline solutions) and the assumption of an acidic point of zero charge (PZC) for the zeolite surface [13,19]. This last consideration can be done on the basis of the observed decrease in the impregnation solution pH from ~ 4.0 to 3.4 when it is contacted with HZSM-5 zeolite. However, the presence of monomeric tungsten species was attributed to their relation with the Brönsted acid sites of the zeolite that enables the simultaneous formation of those species [13]. As an example, in Fig. 3 are comparatively shown the UV DRS of the t-ZW 0.07 sample after impregnation step (Fig. 3b) and in the final form (Fig. 3a). It can be seen that the impregnated sample exhibit two bands at about 220 and 265 nm corresponding to tetrahedral monomeric and octahedral polyoxotungstate species, respectively. However, the spectra of the final t-ZW 0.07 catalyst show only a band at about 230 nm attributed to the monomeric tungsten species. This phenomenon is seen for all the samples except to t-ZW 0.10 and t-ZW 0.20 samples, that posses low amounts of polymeric species (Fig. 2). Thus, the ammonium washing treatment drastically decreases the total W loading of the samples remaining almost exclusively the monomeric W species. This provides additional evidences concerning to the joining of the isolated tetrahedral W species to the Brönsted acid sites of the support surface during the impregnation step. A model of this interaction is showed in Fig. 4. This phenomenon would be analogous to the reported joining of the WO_4 species to the OH groups of silica and alumina [19–21]. Likewise, it has been demonstrated the physical nature of the interaction between

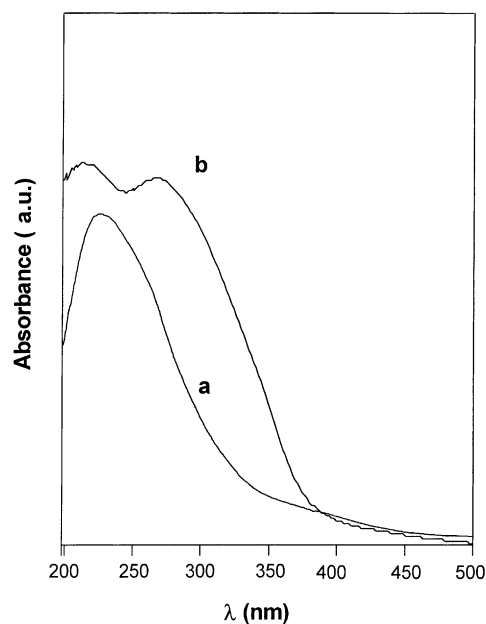


Fig. 3. UV diffuse reflectance spectra of t-ZW 0.07 catalyst: (a) in the final form and (b) after impregnation step.

HZSM-5 surface and the majority of the polytungstate species.

If we consider that the zeolite used in this work shows 0.4 meq OH groups per g, on the basis of a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 90, a maximum load of 1.9% of tungsten can be achieved, with a ratio of two OH groups per W atom. However, the final W loading of the t-ZW samples are substantially lower than this value. This may be attributed to the adsorption in a large extent of polymeric tungsten species during the impregnation stage [13]. Thus, the majority of these latter species, physically adsorbed on the zeolite, are removed by the ammonium washing.

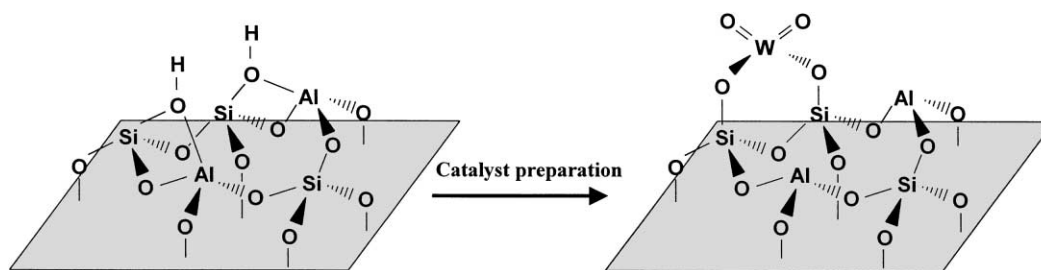


Fig. 4. Model of the joining of the tetrahedral monomeric W species to the Brönsted acid sites of the zeolite.

Taking into account the above assumptions, the characterization results show that the samples with the highest W loading have a certain amount of polymeric species. These species, due to their large size, are located on the external surface of the zeolite causing the blocking of the HZSM-5 channels in some extent. This fact would explain the relatively low BET areas of the t-ZW 0.10 and t-ZW 0.20 catalysts (Table 1). However, in spite of the partial channel blocking, the relative acidity values of these catalysts are similar to those showed by the other samples. It seems that the decrease in acidity due to the pore blocking is counterbalanced by a lesser degree of covering of the zeolite surface by the polymeric species.

Summarizing, the ammonium washing leads to a catalyst series very different from the untreated W/HZSM-5 catalysts. While the treated catalysts contain mainly monomeric species well dispersed with low W loading, the latter exhibit a large amount of polymeric species (polyoxotungstate and WO_3 crystallites), mainly for the highest tungsten contents [13]. This fact was confirmed by means of SEM coupled to energy dispersive X-ray analysis (EDAX). In Fig. 5 are shown the SEM images of treated t-ZW 0.02 and t-ZW 0.20 samples together with that of untreated ZW 11.9 sample. It can be seen that ZW 11.9 catalyst (Fig. 5a) exhibits several polymeric tungsten aggregates of large size on the zeolite crystallites (one of them indicated with an open circle) while these structures are seen in a lower extent (and with lower size) for the t-ZW 0.20 sample (Fig. 5b). The t-ZW 0.02 catalyst (Fig. 5c) does not show any tungsten aggregates on the zeolite surface.

3.3. Methane oxidation tests

The products of the partial oxidation of methane with molecular oxygen over W/HZSM-5 catalysts are HCOH, CO, CO_2 and H_2O . In Table 2 are summarized the catalytic results for all the t-W/HZSM-5 catalysts. For comparison, results from [13] for untreated W/HZSM-5 catalysts and HZSM-5 zeolite are also included in Table 2. The contribution of the homogeneous reaction in the pre-heated zone of the reactor used in this work was reported to be ~ 0.8 mol%, carbon oxides being the unique products formed (mainly CO_2) [14]. This contribution was not

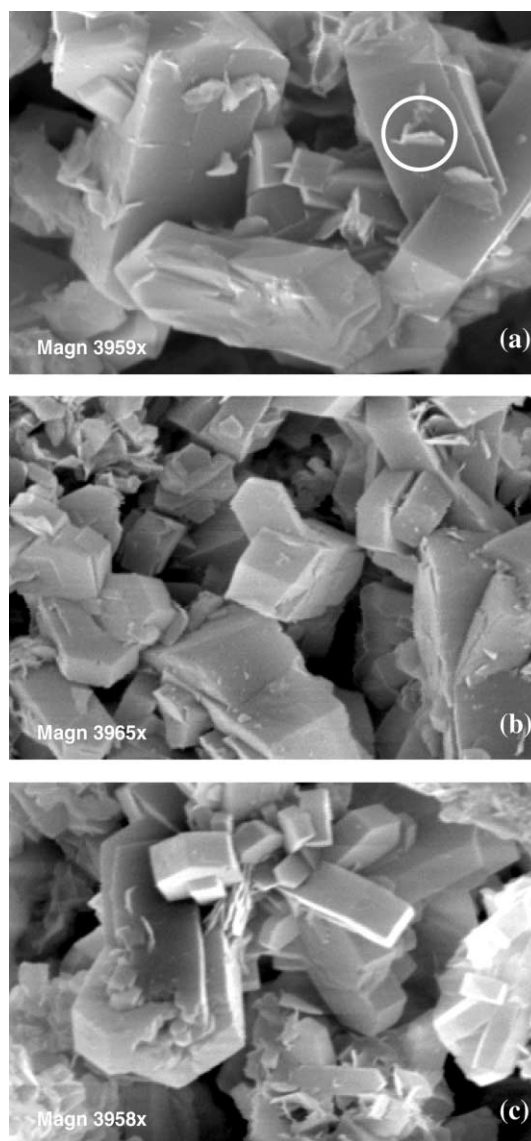


Fig. 5. SEM micrographs of calcined W/HZSM-5 catalysts: (a) ZW 11.9; (b) t-ZW 0.20; (c) t-ZW 0.02.

taken into account in the methane conversion values since it is equal for all the runs.

We have reported the activity of the acid sites of the HZSM-5 on methane conversion leading to the total oxidation products (mainly CO) [13]. Likewise, catalytic results from both W/HZSM-5 catalyst series clearly point out that the active sites for formaldehyde production are located on the supported tungsten

Table 2
Methane conversion and product selectivities for methane partial oxidation over W/HZSM-5 catalysts

| Catalyst | CH ₄ conversion (mol%) | Selectivity (mol%) | | | STY _{HCOH} ^a (g kg _{cat} ⁻¹ h ⁻¹) |
|----------------------|-----------------------------------|--------------------|------|-----------------|---|
| | | HCOH | CO | CO ₂ | |
| t-ZW 0.02 | 10.3 | 9.2 | 50.7 | 40.1 | 27.3 |
| t-ZW 0.05 | 10.5 | 11.0 | 51.1 | 37.9 | 26.8 |
| t-ZW 0.06 | 10.9 | 14.2 | 45.8 | 40.0 | 50.0 |
| t-ZW 0.07 | 10.3 | 15.6 | 46.3 | 38.1 | 52.4 |
| t-ZW 0.10 | 10.8 | 8.3 | 49.6 | 42.3 | 28.6 |
| t-ZW 0.20 | 11.2 | 12.0 | 51.6 | 36.4 | 43.4 |
| HZSM-5 ^b | 11.4 | – | 66.7 | 33.3 | – |
| ZW 0.8 ^b | 9.8 | 3.5 | 25.0 | 71.6 | 11.1 |
| ZW 2.4 ^b | 9.4 | 5.2 | 35.1 | 59.6 | 15.8 |
| ZW 4.0 ^b | 11.0 | 4.6 | 41.3 | 54.1 | 16.3 |
| ZW 7.1 ^b | 11.3 | 4.9 | 41.0 | 54.1 | 17.9 |
| ZW 9.5 ^b | 11.0 | 4.8 | 47.2 | 48.0 | 17.1 |
| ZW 11.9 ^b | 11.9 | 4.1 | 46.0 | 49.9 | 15.8 |

^a Formaldehyde space time yield.

^b Data from [13]. Reaction conditions: $T = 650^\circ\text{C}$; space velocity, $W/F = 7.41 \text{ g h mol}^{-1}$; molar ratio $\text{CH}_4/\text{O}_2 = 5.3$.

oxide phase. Methane conversion values obtained with the t-W/HZSM-5 catalysts are slightly lower than that of HZSM-5. This fact can be attributed to the partial covering of the HZSM-5 active sites with tungsten species less active for methane conversion. With respect to untreated catalysts, this effect is seen only for the low loaded samples. For higher contents the existence of more active tungsten species counterbalances the blocking of the active sites of the zeolite [14].

The most important difference between the catalytic performances of the two catalyst series arises from the selectivity to formaldehyde. As seen in Table 2, t-ZW catalysts exhibit HCOH values up to three times higher than those of untreated ones. It is especially remarkable the high value obtained for the t-ZW 0.02 sample in spite of its low tungsten loading. So, it can be said that the treatment of the catalyst has achieved the proposed object, i.e. the almost exclusively occurrence of tungsten species specific for formaldehyde production from methane. As a result, the formaldehyde space-time yields obtained for t-ZW catalyst series are substantially higher than those of the ZW samples, reaching values around to 50 g HCOH per kg of catalyst and per hour.

With respect to the selectivity to carbon oxides, it can be seen (Table 2) that, in general terms, t-ZW samples show higher CO selectivity values than ZW catalyst series. Likewise, for t-ZW catalyst series,

selectivity to carbon dioxide is meaningfully lower than that of untreated catalyst. These facts will be adequately discussed later.

3.4. Relationship between structure and catalytic activity

The main differences between the catalytic features of both W/HZSM-5 catalyst series have been pointed out above, nevertheless, a more detailed analysis of the results may be made taking into account the great variation in the tungsten loading of the catalysts. The catalytic results have been defined in terms of specific surface activity (SSA, mol CH₄ converted per m² s) and formaldehyde turnover frequency (TOF_{HCOH}, mol HCOH produced per mol W s). The formaldehyde turnover frequency values have been calculated assuming that all the supported metal is active.

In Fig. 6A and B are shown the SSA values vs. tungsten loading for t-ZW and ZW catalyst series, respectively. The SSA value of HZSM-5 zeolite is also indicated in the two graphs. It can be seen that, for t-ZW catalysts with tungsten contents higher than 0.07 wt.% (Fig. 6A), the SSA of the samples increases very slightly with the presence of the tungsten oxide phase. However, for ZW series, SSA of the zeolite is significantly enhanced when tungsten loading increases above 2.4 wt.% (Fig. 6B). It has been reported

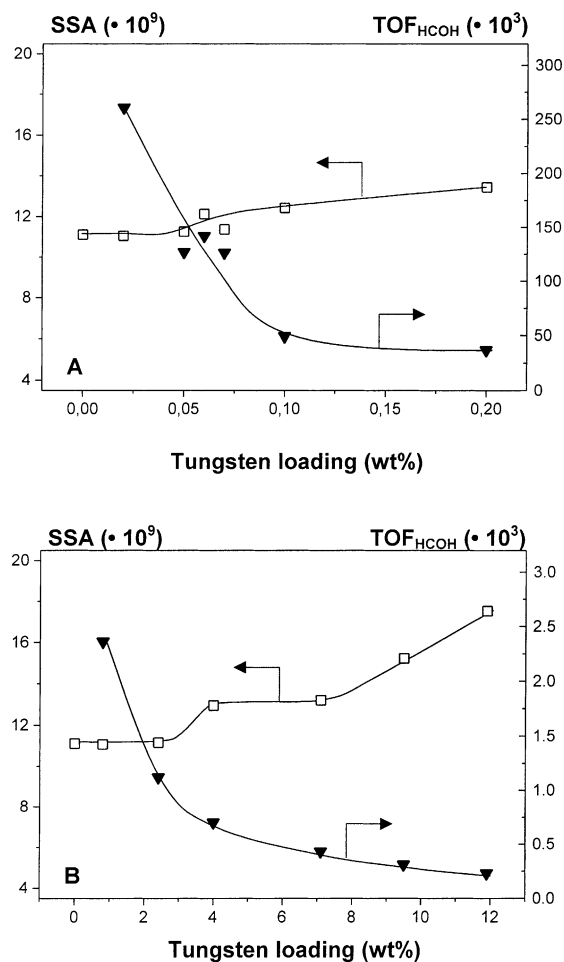


Fig. 6. Reaction parameters vs. tungsten loading for the two W/HZSM-5 catalyst series: specific surface activity (SSA) (\square) and formaldehyde turnover frequency (TOF_{HCOH}) (\blacktriangledown). (A) Catalyst t-ZW series; (B) ZW series. Reaction conditions: $T = 650^\circ\text{C}$; $W/F = 7.41 \text{ g h mol}^{-1}$; $\text{CH}_4/\text{O}_2 = 5.3 \text{ M}$. SSA expressed as mol CH_4 converted per $\text{m}^2 \text{ s}$; TOF_{HCOH} expressed as mol HCOH produced per mol W s.

that reducibility of the supported metal oxide phase is the key for the oxygen activation and, subsequently, for methane activation in these type of catalysts [4,5,14]. According to this assumption, for ZW catalysts, the observed high reducibility of the tungsten oxide overlayer (which covers the active sites of the zeolite surface in large extent) leads to a significant improvement in the SSA of the HZSM-5 [14]. Respect to t-ZW catalyst series, the low W loading of the samples causes

that the majority of the active sites of the zeolite are not covered by the tungsten species. Moreover, the low reducibility of the highest loaded t-ZW samples (Fig. 1) hardly improves the SSA of the zeolite.

In Fig. 6, it can be seen that formaldehyde turnover frequency values of the t-ZW series (Fig. 6A) are up to two orders of magnitude higher than those of the ZW series (Fig. 6B). This fact can be attributed to two reasons: (i) the aggregation of the polymeric species in ZW samples drastically decreases the number of exposed tungsten sites and (ii) monomeric tungsten species existing in the treated catalysts are more active and selective in formaldehyde production. It has been reported the specificity of the $\text{M}=\text{O}$ sites ($\text{M} = \text{Mo}, \text{W}, \text{V}$) of terminal atoms in metal oxide crystallites or isolated monomeric species in the selective production of HCOH from methane over MoO_3 , WO_3 and V_2O_5 silica supported catalysts [3,7,9–12,14,15]. Data presented here clearly agree with this assumption. Likewise, in Fig. 6A it can be observed that formaldehyde TOF values decrease as tungsten loading increases. Again, it is a result of the presence of polyoxotungstate species in some extent.

The discrepancies pointed out above concerning to the carbon oxides selectivities for the two W/HZSM-5 catalyst series can be derived from the different degree of surface covering. Thus, since t-ZW catalysts exhibited higher amount of HZSM-5 acid sites exposed, the CO selectivity values are higher than those of ZW catalyst series. As a result, CO_2 selectivity values for t-ZW catalysts are lower than those of ZW ones.

4. Conclusions

The treatment of impregnated W/HZSM-5 catalysts with an ammonia aqueous solution prior to the calcination step yields to catalysts almost exclusively constituted of monomeric W species. The characterization results let us to assume that these species are chemically joined to the zeolite surface and, therefore, well dispersed. These catalysts have been used in the partial oxidation of methane improving meaningfully the formaldehyde yields obtained by the authors for conventional aqueous impregnated W/HZSM-5 catalysts. Thus, the formaldehyde selectivity values obtained for treated W/HZSM-5 catalysts are up to three times higher than those of untreated ones. These

results are in agreement with the reported hypothesis about the specificity of monomeric tungsten species in the formaldehyde production.

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