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Molybdenum and tungsten dioxides, XO_2 ($X = Mo, W$), as reforming catalysts for hydrocarbon compounds

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Abstract

The reforming catalytic properties of tungsten and molybdenum dioxides have been interpreted in terms of a bifunctional mechanism. A stable XO_2 ($X = W, Mo$) has been obtained following the reduction of XO_3 by hydrogen for 4 h at 400°C for Mo and 460°C for W. A relatively high selectivity up to 100% in isomerization products for the hexanes were obtained at reaction temperatures of 280°C in the case of MoO_2 and at 300°C for WO_2. Titanium dioxide, TiO_2, was chosen as the appropriate support on the basis of its electronic structure which enables to avoid a strong metal–support interaction with the active XO_2 phase.

Keywords: Tungsten dioxide; Molybdenum dioxide; Reforming catalysts; Bifunctional mechanism; Isomerization of hydrocarbons

1. Introduction

Recent catalytic studies on partially reduced bulk MoO_3 and WO_3 systems using 2-methylpentane (2MP) reactant revealed considerable catalytic activities in terms of isomerization reactions with 3-methylpentane (3MP) and *n*-hexane (*n*H) as the major products. Similar results were obtained using bulk MoO_2 and WO_2 or partially oxidized Mo(0) and W(0) systems [1–3]. The identification of the active catalytic species were obtained using UPS and XPS techniques as MoO_2 and WO_2. In the case of MoO_2, e.g., the two free 4d electrons per Mo atom participate in σ and π bond formation between the two adjacent Mo atoms along the *c*-axis. The conjugation of these π electrons imparts the metallic properties (MoO_2 and WO_2 are conductors) observed by UPS and XPS in form of density of states (DOS) at the Fermi level [4]. The similarities between these dioxides and Pt deposited on acidic alumina could be summarized as follows. The conjugated and delocalized π electrons act like Pt particles in terms of H_2 and C–H bond dissociation. Moreover, the produced hydrogen atoms lead to the formation of Brönsted acid X–OH function(s) which play the role of the acidic alumina.

In this work, we present the reforming catalytic properties of XO_2 ($X = W, Mo$) phase prepared in situ by a controlled hydrogen reduction of either bulk XO_3 or commercial XO_2 (partially oxidized to XO_3 on the surface). The isomerization reactions of certain hexanes were studied in function of the reaction temperature. The presence and the stability of the XO_2 phase is monitored in function of the highest selectivity in isomerization products following the reduction of the initial XO_3 phase by hydrogen in function of temperature. Obviously, the reduction temperature of XO_3 and its duration depend on the nature of the metal, Mo or W. For example, in the case of bulk MoO_3 or commercial MoO_2 (partially oxidized to MoO_3 on the surface) it required 4 h of reduction under H_2 at 400°C

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and only 1 h for the equivalent five layers of MoO_3 deposited on TiO_2 in order to get the stable and active MoO_2 phase. The stability of these surfaces has been tested by repeated injections of the hydrocarbon reactant for more than 60 h with no changes in activity or selectivity. Once the active XO_2 phase is obtained, it is possible to study the catalytic activity of a hydrocarbon reactant by varying the reaction temperature without exceeding 400°C for MoO_2, for example.

2. Experimental

Molybdenum trioxide (99.998%), MoO_2 (99%), WO_3 (99.9%) and $(NH_4)_6H_2W_{12}O_{40}\cdot 4H_2O$ were obtained from STREM Chemicals. TiO_2 is Degussa P-25 (20% rutile) with pore volume of 0.5 cm^3/g and BET surface area of $50\pm 5\ m^2/g$. Supported WO_3/TiO_2 catalyst was prepared by impregnating the right amount of W contained in its corresponding salt following the method described by Ipatieff and coworkers [5]. The catalytic experiments were performed using 50 mg of the bulk or the supported catalysts and a hydrogen flux of 30 cm^3/min at fixed temperature and atmospheric pressure. A dose of 5 μl of reactant (partial pressure = 5 Torr) was injected periodically. The catalytic products were analysed by gas chromatography. The reaction temperature in this work is always 350°C unless it is mentioned otherwise. Elemental analysis of the sample was made at the "Service Central d'Analyse" de Vernaison-CNRS (France).

3. Results and discussion

The results concerning the reforming catalytic properties of the XO_2 (X = W, Mo) in the bulk state as prepared by the partial reduction of XO_3 or deposited on TiO_2 will be presented.

3.1. Tungsten trioxide

Tungsten trioxide, WO_3, sample as received did not show any catalytic activity for the 2MP reactant. It required at least 4 h of reduction under H_2 atmosphere at 400°C in order to observe a considerable activity in terms of isomerization process, a maximum conversion of 32.5% and a selectivity of 88.3% in isomerization products; mainly 3MP and *n*H at 350°C reaction temperature were obtained after at least 4 h of reduction by hydrogen at 460°C. The catalytically active phase has been identified by XPS and UPS as WO_2.

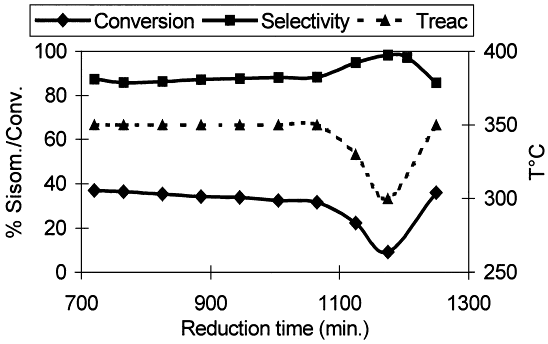

Fig. 1. The catalytic activity and selectivity of 2MP in function of time and reaction temperature on WO_2 prepared by hydrogen reduction of WO_3 at 460°C.

Once this active WO_2 phase is prepared, it seems to be stable in function of time under the experimental conditions. Consequently, it is possible to study the catalytic process at different reaction temperatures without altering the surface chemical structure. A conversion of 9.2% and a selectivity of 98.4% in isomerization products mainly 3MP and *n*H were obtained for the 2MP reactant at 300°C reaction temperature. A considerable increase in conversion to 37% with a slight decrease in selectivity to 87.5% were obtained at 460°C reaction temperature. The conversion and selectivity values are completely reproducible in the range of reaction temperatures up to 460°C as presented in Fig. 1. However, at higher reaction temperatures, a considerable increase in conversion in favour of hydrogenolysis products, mainly C1, C2 and C3 was observed. The reduction of WO_3 at higher temperatures leads to the formation of the metallic W(0) state, as revealed by XPS measurements, responsible for the hydrogenolysis process.

In the case of *n*H reactant, a conversion of 24% and a selectivity of 85% in 2MP and 3MP (2MP/3MP = 1.7) isomerization products were obtained at 350°C reaction temperature. It is interesting to note that the WO_2 phase shows an important activity for the unsaturated hydrocarbon reactants at relatively low reaction temperatures. A conversion of 26% and a selectivity of 99% in isomerization products were obtained at 250°C for the 4-methylpentene-1 reactant.

Table 1
Conversion, selectivity and products distribution of *n*H reactant in function of the reaction temperature using MoO_2 catalyst

Reaction temperature (°C)	280	300	320	340	360	380	400
Conversion (%)	3.9	8.2	16.1	20.2	34.7	47.4	63.3
Selectivity (isomerization)	97.4	94.3	86.4	84.8	77.4	61.5	46.0
Distribution (isomerization products, %)							
22DMB	1.0	1.6	1.9	1.8	1.8	2.0	1.2
23DMB	10.6	8.7	8.1	8.1	7.4	5.4	4.4
3MP	33.2	31.1	28.2	27.7	26.0	21.7	16.1
2MP	56.5	54.2	48.5	47.8	42.6	31.9	23.7
Distribution (cracking products, %)							
C1	0	0.5	4.8	3.5	3.9	5.3	14.2
C2	0	1.8	0.1	1.5	2.5	4.0	10.2
C3	2.9	3.4	7.8	8.1	10.8	11.2	15.6
C4	0	0	0.9	1.1	2.6	3.5	7.5
C5	0	0	0	1.0	2.6	14.5	6.6
2MP/3MP	1.7	1.8	1.7	1.7	1.6	1.5	1.5

3.2. *Molybdenum trioxide*

Molybdenum trioxide sample as received did not show any catalytic activity in similar way to that observed in the case of tungsten trioxide. It required 4 h of reduction under hydrogen at 400°C in order to get a stable state of MoO_2 phase at the sample surface. A conversion of 37.2% and a selectivity of 78.8% in isomerization products, mainly 3MP and *n*H ($3MP/nH = 1.03$) was observed using the 2MP reactant at 350°C reaction temperature. These results are relatively close to what was observed in the case of WO_2 prepared by the reduction of WO_3.

The catalytic properties of the already prepared MoO_2 system has been studied for the *n*H reactant at reaction temperatures between 280 and 400°C and are presented in Table 1.

As could be observed from the catalytic results in Table 1, the conversion increases in function of the reaction temperature increase while the selectivity in isomerization products decreases. This selectivity becomes 46% at 400°C as compared to 97% at 280°C. The decrease in selectivity is in favour of C1, C2 and C3 hydrocracking products. It is interesting to note that the major isomerization products 2MP and 3MP are present in the reaction temperatures range between 280 and 400°C with a ratio $2MP/3MP \approx 1.7$ which corresponds to the thermodynamic equilibrium.

Continuous reduction of MoO_3 by hydrogen at temperatures equal to or higher than 500°C leads to the formation of the metallic Mo(0) state as observed by XPS. In this case, only extensive hydrogenolysis products for the different hexane reactants were obtained at 350°C reaction temperature. Moreover, it was not possible to obtain isomerization products on this metallic surface regardless of the reaction temperature contrary to what was observed in the case of MoO_2.

4. Deposited tungsten and molybdenum dioxides on TiO_2

In order to increase the surface area of the active XO_2 phase and maintain its electronic structure, titanium dioxide was found to be the appropriate support on the basis of its semiconductor electronic properties and its crystal structure. The absence of strong metal–support interaction is confirmed by XPS measurements of the supported sample. A well-defined WO_2 phase was obtained following the reduction of the deposited WO_3 on TiO_2 in similar way to bulk WO_3. This is not possible when other supports such as Al_2O_3 or SiO_2 were used. The new bond formation between the two free electrons per W or Mo atom in XO_2 with the relatively active surfaces Al_2O_3 or SiO_2 (strong metal–support interaction) leads to the tungsten or molybdenum complex formation, inactive for the isomerization reactions of alkanes.

An equivalent of five monolayers of WO_2 were deposited on TiO_2 by impregnating the exact amount of

Table 2
Conversion, selectivity and products distribution of 2MP reactant in function of the reaction temperature using five layers of WO_2 deposited on TiO_2 catalyst

Reaction temperature (°C)	300	315	330	350	380	400	420	460
Conversion (%)	1.2	2.2	3.6	7.7	13.3	14.8	15.7	25.8
Selectivity (isomerization)	100	98.2	97.5	91.3	84.2	68.8	48.8	15.0
Distribution (isomerization products, %)								
22DMB	0	1.6	2.2	1.9	1.8	1.5	1.0	0.3
23DMB	18.3	18.4	13.9	10.4	10.1	8.6	6.5	2.0
3MP	65.8	62.9	64.8	60.0	47.9	33.2	22.9	6.9
*n*H	15.9	15.4	16.8	18.7	24.4	24.5	17.4	3.0
MCP	0	0	0	0.2	0	0.3	0.4	0.1
CC6	0	0	0	0	0	0.2	0.6	2.8
Distribution (cracking products, %)								
C1	0	0	0.2	0.3	1.4	3.2	8.7	37.5
C2	0	0.1	0.1	0.1	0.6	2.0	5.7	18.8
C3	0	0.5	0.6	2.0	4.3	8.4	12.5	12.6
C4	0	0.3	0.5	2.5	4.5	9.3	13.5	10.5
C5	0	0.8	1.1	3.8	5.0	8.9	11.0	5.7
3MP/*n*H	4.1	4.1	3.9	3.2	2.0	1.4	1.3	2.3

tungsten present in its $(NH_4)_6H_2W_{12}O_{40}\cdot 4H_2O$ salt. Tungsten is converted to WO_3 by calcination at 500°C for 16 h. A reduction of the WO_3 phase present on the TiO_2 surface by hydrogen at up to 510°C enabled to obtain a well-defined WO_2 state as observed by XPS. The catalytic properties of this supported system were studied using 50 mg of the catalyst (22% W) for the 2MP reactant at reaction temperatures up to 460°C (see Table 2).

It is very interesting to note that a relatively high selectivity in isomerization products with reasonable conversions was obtained at reaction temperatures between 300 and 380°C. Although the conversion gradually increases at higher reaction temperatures to reach 25.8% at 460°C, the selectivity decreases considerably to 15% at this temperature. From reaction products distribution presented in Table 2, it could be clearly observed that C1 and to lesser extent C2 and C3 constitute the major hydrocracking products at 460°C reaction temperature.

In the case of molybdenum dioxide deposited on TiO_2, a similar preparation method to that of WO_2/TiO_2 has been followed. The five monolayers of MoO_3 deposited on TiO_2 were reduced by hydrogen at 400°C for 2 h in order to convert it to the active MoO_2 phase. The 2MP and *n*H reactants were studied using this supported MoO_2/TiO_2 catalyst at reaction temperatures up to 400°C. A very high selectivity in isomerization products close to 98% with 10% in conversion was obtained for the 2MP reactant at reaction temperatures between 280 and 300°C. A similar trend to WO_2/TiO_2 in terms of continuous decrease in selectivity in isomerization in favour of hydrocracking products as the reaction temperature increases has been observed. A comparison between the two MoO_2- and WO_2-supported catalysts activities for the 2MP reactant at 400°C reaction temperature reveals that higher selectivity of 68.8% with a conversion of 14.8% were obtained in the case of WO_2/TiO_2 as compared to 39.6% in selectivity and 65.3% in conversion for MoO_2/TiO_2. This different catalytic behaviour between the two systems could be attributed in part to different metallic and acid properties of the two systems.

The catalytic behaviour of the supported MoO_2/TiO_2 for the *n*H reactant is very similar to the bulk system in terms of high selectivity in isomerization products at reaction temperatures between 280 and 340°C. However, the two systems behaviour differs at higher reaction temperature as could be observed, e.g., at 400°C where the selectivity of the supported system is 22.7% as compared to 46% for the bulk MoO_2.

A comprehensive study taking into consideration the relation between the different reaction parameters, the catalyst surface porosity, surface area, its electronic structure and acidic properties as well as the nature of the reactants is under way.

5. Conclusion

The catalytic activities of the XO_2 ($X = W, Mo$) systems for the isomerization reactions of alkanes were interpreted in terms of a bifunctional mechanism. The active XO_2 phase is prepared in situ following the reduction by hydrogen of the surface XO_3 or commercial XO_2 which is covered by few monolayers of XO_3 on the surface. The reduction temperature was 400°C for 4 h in the case of molybdenum and 460°C for tungsten. The reforming catalytic properties of these XO_2 systems were studied for different saturated hexanes at different reaction temperatures. A selectivity of almost 100% in isomerization products was obtained for *n*H and 2MP at 280°C reaction temperature for MoO_2 and 300°C for WO_2. At higher reaction temperatures it was observed that considerable increase in conversion is associated with a constant increase in hydrogenolysis products. This is attributed in part to kinetic effects.

Titanium dioxide was found to be the appropriate support for the active XO_2 phase which enables to increase the catalytic surface area without altering its catalytic properties. The reforming catalytic properties of the XO_2 as a bulk or deposited on TiO_2 systems were completely stable and reproducible under the experimental conditions carried out in this work.

References

[1] A. Katrib, P. Leflaive, L. Hilaire, G. Maire, Catal. Lett. 38 (1996) 95–99.
[2] A. Katrib, V. Logie, N. Saurel, P. Wehrer, L. Hilaire, G. Maire, Surf. Sci. 377–379 (1997) 754–758.
[3] A. Katrib, V. Logie, M. Peter, P. Wehrer, L. Hilaire, G. Maire, J. Chim. Phys. 94 (1997) 1932–1937.
[4] A. Gulino, S. Parker, F.H. Jones, R.G. Egdell, Chem. Soc. Faraday Trans. 12 (1996) 2137–2141.
[5] H. Pins, R.C. Oberg, V.N. Ipatieff, J. Am. Chem. Soc. 70 (1948) 533.