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CATALYTIC PROPERTIES OF SUPPORTED TUNGSTEN OXIDE CATALYSTS

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Catalytic properties of the WO_3-MgF_2 preparations obtained by the impregnation (I-series) and coprecipitation (C-series) method have been determined in acid environment. Various tungsten complexes causing the Lewis and Broensted acidity have been observed by IR spectroscopy. For catalysts of the I-series the isolated tungsten species were responsible for the activity in acid reactions, whereas for the C-series preparations the polymerized oxide was also involved.

1. Introduction

Properties of supported transition metal oxide active phases may be modified by interaction with the support. Although in recent years, many papers have been devoted to studies of the WO_3/Al_2O_3 [1–5], the structure of tungsten oxide surface complexes still remains unclear. The results obtained on non-oxidic supports may provide additional information about the structure of the dispersed tungsten species. Magnesium fluoride was used as the support in this work since it had been found previously that MoO_3 [6–8] or V_2O_5 [9] supported on its surface generates new acid-base and redox sites active in different catalytic reactions.

The aim of this work was the determination of the influence of WO_3 on catalytic properties of the WO_3-MgF_2 samples, obtained with the impregnation or coprecipitation method in acid environment.

2. Experimental

PREPARATION OF CATALYSTS

Two series of WO_3-MgF_2 catalysts were prepared, one by impregnation (I_A) and one by coprecipitation (C_A).

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Preparations of the I_A-series were obtained by mixing MgF_2 powder of 0.25–0.5 mm grain size preheated at 400 ° C for 5 hrs, to fluoric acid solution of tungstic acid. The solution was taken in an amount sufficient for incipient wetness to be observed. The preparations were then first dried at 50 ° C with frequent stirring, then at 105 ° C for 24 hrs and finally annealed at 400 ° C for 4 hrs. The solutions taken for impregnation contained amounts of tungstic acid which corresponded to the surface coverage of MgF_2 equal to 0.1, 0.2, 0.5 and 1.0 monolayer of tungsten oxide.

Preparation of the C_A-series were prepared by mixing a freshly precipitated MgF_2 with a solution of tungstic acid in 40 % fluoric acid. Details of the experimental procedure were described in [6,9]. Using the solutions of tungstic acid of different concentrations we obtained preparations with W/Mg atomic ratio between 0.1 and 0.25.

INFRARED SPECTRA

IR spectra in the range of 650–1100 cm^{-1} were determined with a BRUCKER IFS 113 v spectrometer. The samples were prepared by grinding 2 mg of the catalyst with 0.2 g KBr and pressing the powder into thin discs at 8 ton/cm^2. Fig. 1 shows IR spectra of the WO_3-MgF_2 catalysts after subtracting the contribution of MgF_2.

The stretching vibration spectra of the OH groups as well as the stretching and deformation vibrations of adsorbed pyridine were obtained with a Perkin Elmer 580 Spectrometer. Further steps of the experimental procedure were similar to that described in [9].

CATALYTIC ACTIVITY

The catalytic properties of the samples were determined with the pulse microreactor technique for the following reactions:

a) Isomerization of 1-butene;
Reaction temperature–120 ° C for I and C-series;
catalyst weight–0.1 g;
1-butene (gas) volume/pulse size–0.5 cm^3 for I and C-series;
flow rate of helium carrier–30 cm^3/min;
GC column: 10 m propylene carbonate at 0 ° C.

b) Skeletal isomerization of cyclohexene;
Reaction temperature–370 ° C for I and C-series;
catalyst weight–0.1 g;
cyclohexene (liquid) volume/pulse size–0.4 μl for I and 1.6 μl for C-series;
flow rate of helium carrier–20 cm^3/min;
GC column, 2 m propylene carbonate at 25 ° C.

c) Decomposition of 2-propanol;
Reaction temperature–300 °C for **I**-series and 140 °C for C-series;
catalyst weight–0.01 g;
isopropanol (liquid) volume/pulse size–0.2 μl;
flow rate of helium carrier–30 cm^3/min;
GC column, 1 m Emulphor 0 at 65 °C.

d) Cumene cracking;
Reaction temperature–370 °C for I and C-series;
catalyst weight–0.1 g;
cumene (liquid) volume/pulse size–0.4 μl for I and C-series;
flow rate of helium carrier–25 cm^3/min;
GC column 1 m Emulphor 0 at 100 °C.

3. Results and discussion

Table 1 summarizes the chemical composition of preparations and their surface areas determined by the BET method from the adsorption isoterms of nitrogen at liquid nitrogen temperature. Impregnation of MgF_2 with tungstic acid did not influence its surface area. Contrary to that coprecipitation had a profound influence on the surface area. An increase in surface area was explained by the peptization effect as in [9].

Fig. 1 presents IR spectra of the investigated samples. C_A-MFW_1 preparation exhibit the following bands: 710, 750, 765, 820, 880-910 and the outlines of bands at 1010 and 1050 cm^{-1}. For the C_A-MFW_5 sample intensity of the bands at 820,

Table 1
Characteristics of WO_3-MgF_2 preparations

Impregnated					
Preparation	MF	I_A-$MFW_{0.1}$	I_A-$MFW_{0.3}$	I_A-$MFW_{0.7}$	I_A-$MFW_{1.5}$
Atomic ratio (W/Mg)	0.000	0.001	0.003	0.007	0.015
MgF_2 surface coverage with W, (monolayers)	0.0	0.1	0.2	0.5	1.0
Surface area, (m^2/g)	30	30	30	29	31
Coprecipitated					
Preparation	WO_3	C_A-MFW_1	C_A-MFW_5	C_A-MFW_{10}	C_A-MFW_{18}
Atomic ratio (W/Mg)	0.0	0.01	0.05	0.10	0.18
Surface area (m^2/g)	3	44	79	60	53

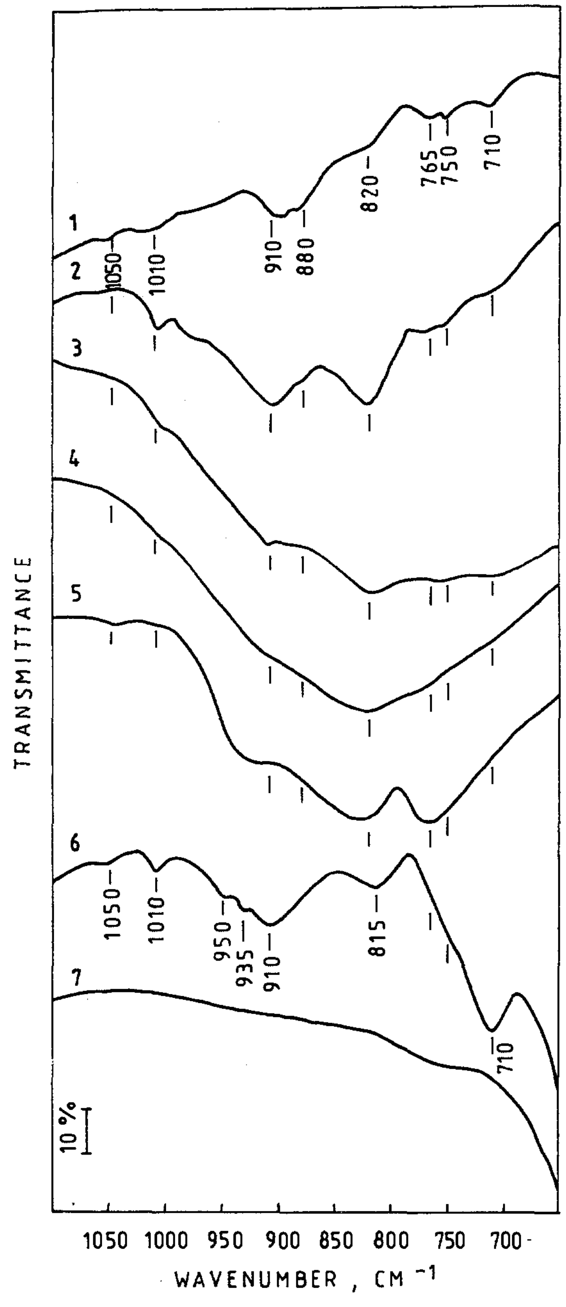

Fig. 1. IR spectra of the WO_3-MgF_2 catalysts. C_A-MFW_1 (1), C_A-MFW_5 (2), C_A-MFW_{10} (3), C_A-MFW_{18} (4), WO_3 (5), I_A-$MFW_{1.5}$ (6), MgF_2 (7).

910 and 1010 cm^{-1} increases distinctly while intensity of the remaining bands decreases. For catalysts with the atomic ratio 10 and 18 W/Mg (spectra 3 and 4 respectively in fig. 1) a clear broad band at 650–900 cm^{-1} was observed. This

broad band is characteristic for WO_3 [10]. For preparation I_A-$MFW_{1.5}$ (spectrum 6 in fig. 1) one observes the following bands: 710, 815, 910, 935, 950, 1010 and 1050 cm^{-1}. The bands at 710, 750, 765, 820, 880 and 910 cm^{-1} can be assigned to the ν (O-W-O) frequency, the bands at 930 and 950 cm^{-1} to the ν (W = O),

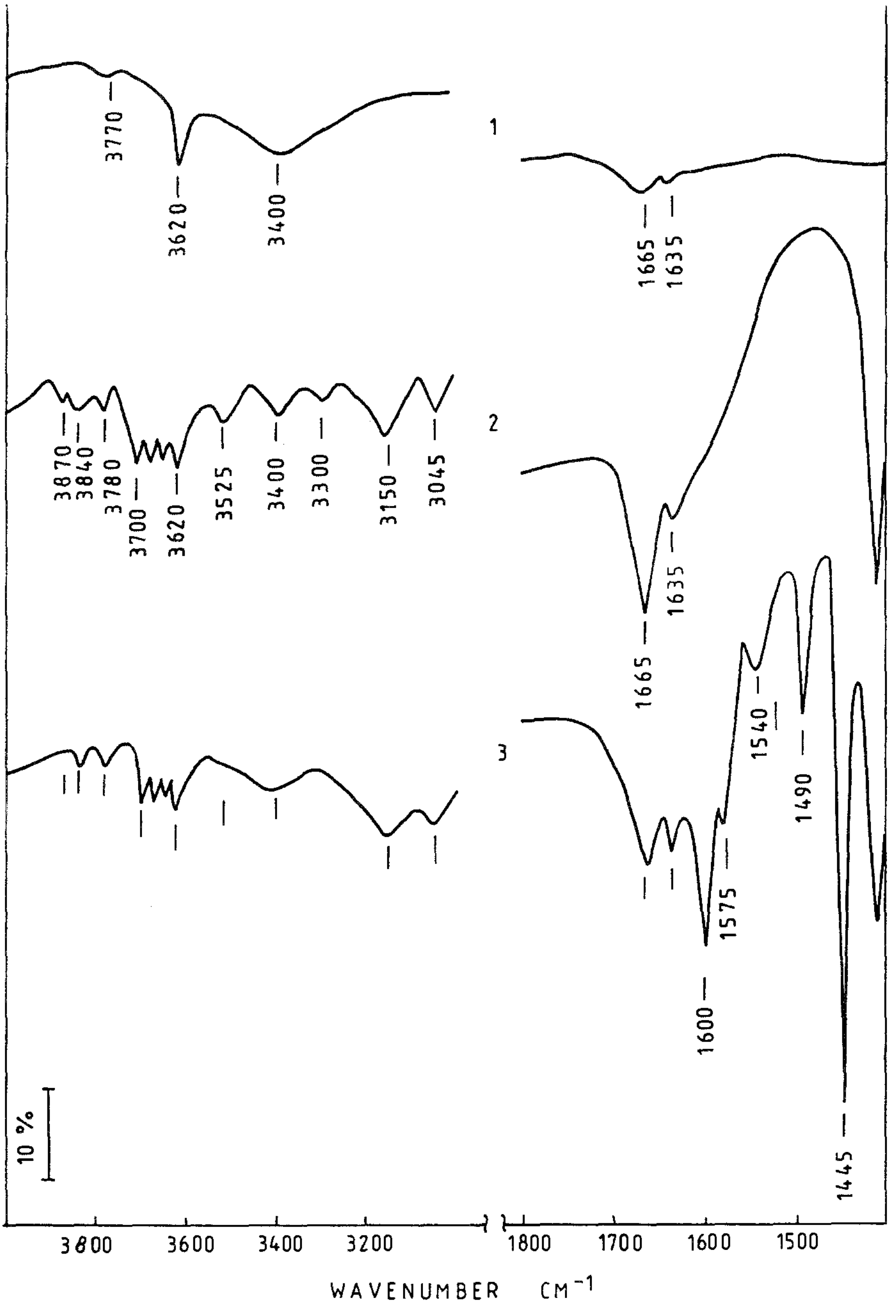

Fig. 2. IR spectra of WO_3-MgF_2 samples before pyridine adsorption: MgF_2 (1), I_A-$MFW_{1.5}$ (2); and after pyridine adsorption: I_A-$MFW_{1.5}$ (3).

whereas the bands at 1010 and 1050 cm^{-1} should be related to the δ (OH) frequency [11]. Bands at 710, 820 and 880 cm^{-1} are also observed for $MgWO_4$ [12]. On the basis of the characteristic vibrations of the tetrahedrally coordinated $[WO_4]$ group and from comparison with the spectra of MgF_2 and WO_3 (spectra 7 and 5 respectively in fig. 1), it may be concluded that the bands at 710, 820 and 880 cm^{-1} originate from the tetrahedral ion $[WO_4]$. These bands were detected in C_A-MFW_1 and C_A-MFW_5. Thus the appearance of these bands may be taken as an indication of the presence of tungstate ions in tetrahedral coordination. Besides the bands characteristic of the $[WO_4]$ ions bands characteristic of WO_3 were also observed, which intensity increases as the W/Mg ratio in the samples increases (spectra 3 and 4 in fig. 1).

X-ray examination of the crystalline structure and lattice constants of MgF_2 before and after introducing the tungstic acid indicates that the tungstic species are located at the surface. This examination reveals the presence of MgF_2 and WO_3 only. It is believed that for a thin coverage of the surface the isolated tetrahedral tungstate complexes are formed (710, 820 and 880 cm^{-1}) which then polymerize into chains or patches of WO_6 octahedra forming WO_3 at the surface of coprecipitated preparations (650–900 cm^{-1}). At the surface of impregnated catalysts beside the hydrated WO_4^{2-} tetrahedral (815 and 935 cm^{-1}) [12] the $WO_3.xH_2O$ [710, (815), 910, 950, 1010 cm^{-1}] [11] complexes are also observed.

Formation of the tetrahedral tungstate complexes and the octahedra clusters of the WO_3 at the surface of the fluoride must cause some changes in structure of the surface hydroxyl groups in MgF_2 itself. Three types of the OH groups exist at the MgF_2 surface [13]. The bands at 3770, 3620 and 3400 cm^{-1} corresponding to these groups linked with the surface Mg ions are shown in fig. 2 (spectrum 1).

Introduction of tungstic acid at the surface of MgF_2 causes the appearance of new bands at: 3870, 3840, 3700, 3670, 3650, 3525, 3300, 3150 and 3045 cm^{-1} (spectrum 2, fig. 2) which are related to the W ions introduced at the surface. The three last bands are assigned to the molecular water linked with WO_3 [11].

Besides the bands originating from OH groups, some other bands situated at 1665 and 1635 cm^{-1} and assigned to the molecular water were also observed. Introduction of tungsten causes a considerable increase in intensity of these bands.

The spectrum of pyridine (Py) adsorbed at the surface of the catalyst (spectrum 3, fig. 2) reveals the acidic properties of the WO_3-MgF_2 samples. The band at 1445 cm^{-1} is a clear indication of Lewis acidity, whereas the presence of Broensted acidity is indicated by the band at 1540 cm^{-1} [14]. Admission of Py causes a disappearance of the 3870, 3525 and 3300 cm^{-1} bands. Hence, hydroxyls corresponding to these bands interact with Py, yielding pyridinium ion. Since the OH groups are not detected at the surface of MgF_2, they are generated by the introduction of W-O polyhedra on the MgF_2 surface. None of the remaining OH groups present on WO_3-MgF_2, i.e., 3840, 3700, 3670 and 3645 cm^{-1}, changed their intensity after Py admission. It may indicate that these OH groups are

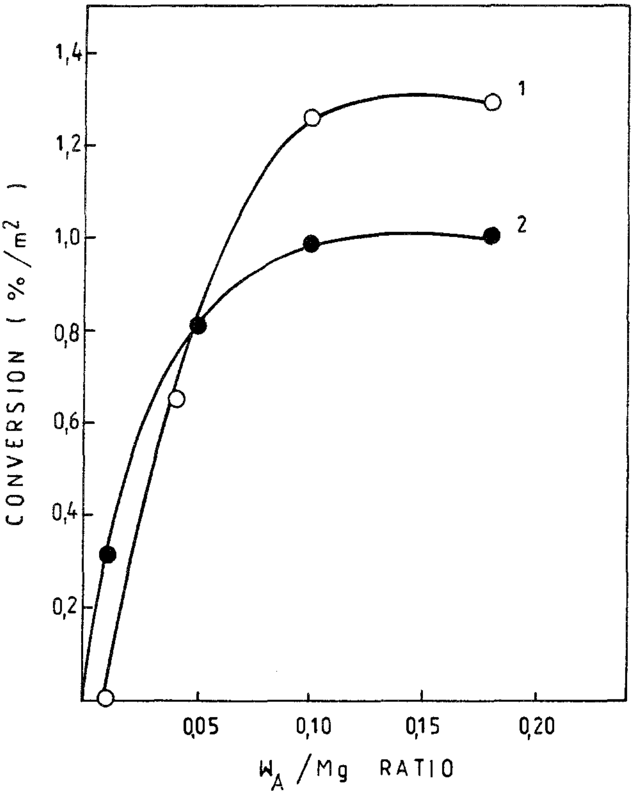

Fig. 3. Catalytic activity of the coprecipitated preparations for cumene cracking (1) and skeletal isomerization of cyclohexene (2) as a function of W/Mg atomic ratio.

weakly acidic or even non-acidic. IR spectra have been measured for both I and C-series. Since they exhibit the same bands, except of bands of molecular water linked to WO_3 observed only in the I preparations, fig. 2 shows an example of I_A-$MFW_{1.5}$.

Therefore it can be concluded that a considerable change in MgF_2 surface properties takes place after introduction of the tungsten ions. Strong Lewis and Broensted acidity appears in the WO_3-MgF_2 preparations. Broensted acidity comes from the OH groups which are hydroxyls bonded to W ions in tetrahedral coordination and hydroxyls connected with WO_3 (bands at 3525 and 3300 cm^{-1}). The Lewis acidity, on the other hand, may result from the presence of coordinatively unsaturated tungsten ions.

The above structural changes have a profound influence on the catalytic properties. Fig. 3 presents the results of catalytic activity for the C-series WO_3-MgF_2 preparations in the cumene cracking (curve 1) and skeletal isomerization of cyclohexene (curve 2). All the samples were active for isomerization, however for cumene cracking, only catalysts with W/Mg 0.01 were active. For atomic ratio W/Mg above 0.1 the level of conversion per m^2 was practically

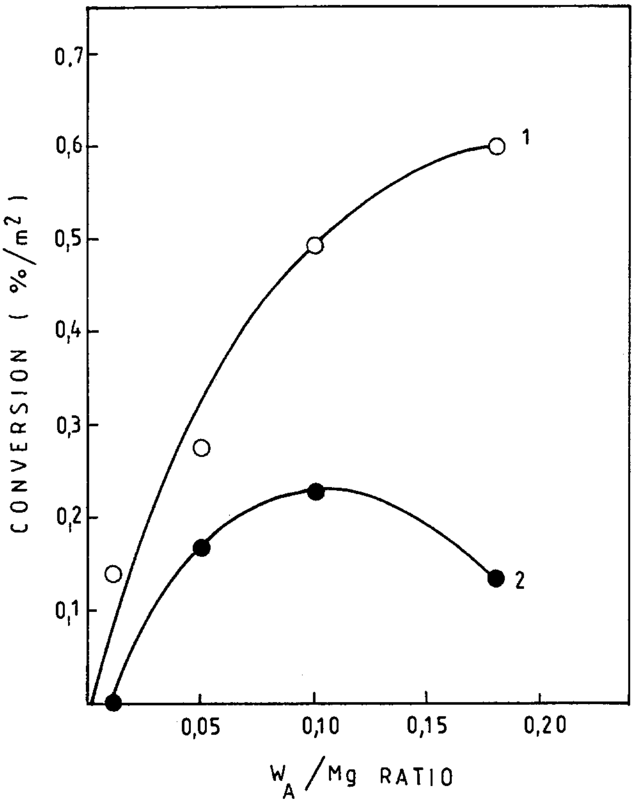

Fig. 4. Catalytic activity of the coprecipitated preparations for 1-butene isomerization (1) and 2-propanol decomposition (2) as a function of W/Mg atomic ratio.

constant for both reactions. This indicates that an increase in tungsten content does not cause an increase of its surface concentration, nor does it enhance the strength of acidic centers. Both these reactions are caused by strong Lewis and Broensted acidic centers but only protonic centers are responsible for the cumene cracking.

The activity of the isomerization of the C-series preparations for reactions of butene-1 (curve 1) and isopropanol decomposition (curve 2) is illustrated in fig. 4.

For isomerization the activity per unit surface area was increasing with increasing amount of introduced tungsten. For the studied catalysts the cis-butene-2/trans-butene-2 ratio amounted to about one so isomerization of butene-1 takes place on acidic centers. The decomposition of propanol was running towards propylene (lack of acetone), so the acidic centers were the active centers (even of low strength).

Fig. 5 presents the catalytic activity of the I-series preparations in reaction of cumene cracking (curve 1) and cyclohexene isomerization (curve 2). For the latter reaction the activity was increasing with increasing amount of tungsten in the catalyst, whereas for cracking reaction only the I_A-$MFW_{1.5}$ sample was active.

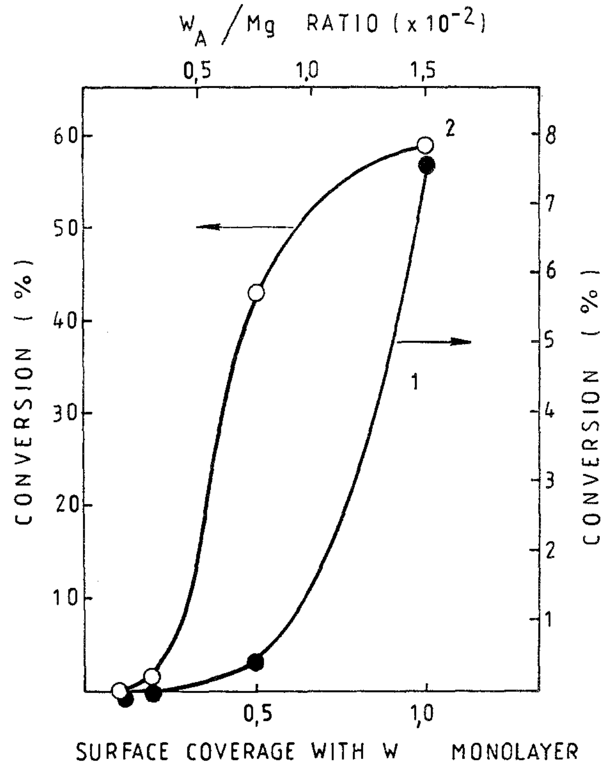

Fig. 5. Catalytic activity of the impregnated catalysts for cumene cracking (1) and isomerization of cyclohexene (2) as a function of surface coverage with W.

The I-series catalysts were also active in reaction of isomerization of butene-1 (curve 1) and decomposition of isopropanol (curve 2, fig. 6). For both these reactions we observed an increase of activity with increasing amount of tungsten, but for isomerization reaction activity appeared only when the coverage exceeded 0.2 of the monolayer.

The above results show that deposition of the monolayer of tungstic oxide on the surface of magnesium fluoride strongly affects the catalytic properties. Gradual increase in the catalytic activity of the I-series preparations, observed while increasing the surface coverage of MgF_2 crystallites with tungsten species, indicates that the isolated tungstate complexes take part in reactions demanding acidic centers. The increase in activity of the C-series preparations with the further surface coverage with tungsten species, revealing itself especially clearly for reaction of the isomerization of 1-butene, proves that the polimerized oxides also participate in catalytic activity.

Comparison of activities of the I and C-series preparations exhibits a clear advantage of the impregnated catalysts. The higher activity is a consequence of more active tungsten species formed on their surface. In the impregnated preparations IR studies showed the existence of the distinct bands assigned to WO_4^{2-}

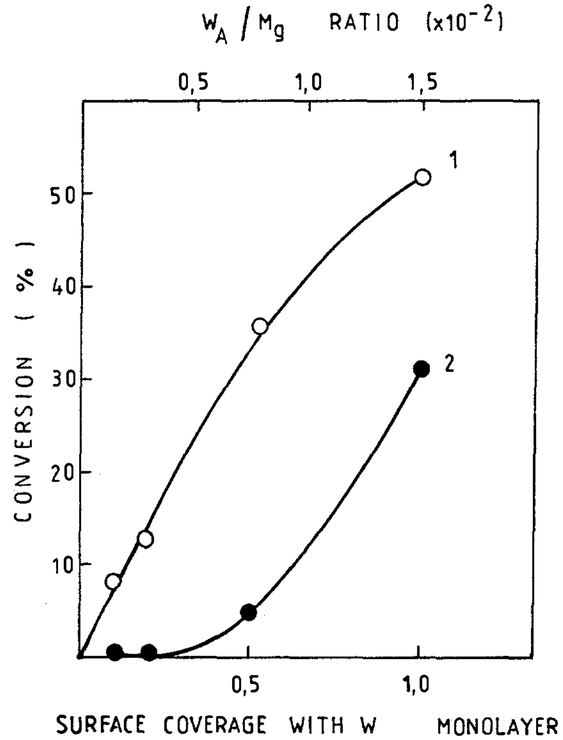

Fig. 6. Catalytic activity of the impregnated catalysts for 1-butene isomerization (1) and 2-propanol decomposition (2) as a function of surface coverage with W.

(aq), whereas in the coprecipitated preparations their characteristic bands were not observed.

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