

n-Pentane Isomerization Catalyzed by Fe- and Mn-Containing Tungstated Zirconia Characterized by Raman Spectroscopy

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Although Fe and Mn promote sulfated zirconia for *n*-pentane isomerization, they do not promote tungstated zirconia. Raman spectra demonstrate the formation of manganese tungstate (and possibly iron tungstate), which likely hinder(s) the formation of highly dispersed oxidic promoters such as those in iron- and manganese-promoted sulfated zirconia. © 2000 Academic Press

Among catalysts for light alkane isomerization, tungstated zirconia (1–7), WO_x/ZrO_2 (WZ), is less active than sulfated zirconia (SZ) at low temperatures (<100°C) but more stable than SZ at high temperatures (8) and in reducing atmospheres (9). Addition of Fe and Mn promoters to SZ, giving FMSZ, increases the activities for low-temperature *n*-butane or *n*-pentane isomerization by orders of magnitude (10–12); the highly dispersed promoter oxides have been suggested to form sites for alkane dehydrogenation, which may initiate isomerization (11, 13).

Our goal was to determine the role of Fe and Mn in WZ and to compare it with the promoter role of Fe and Mn in SZ. Raman spectroscopy was used to test for possible compound formation resulting from reaction of Fe- and Mn-containing precursors with surface tungstate.

WZ, prepared as described (5) and containing 19 wt% WO_3 , was dried at 383 K for 12 h and calcined at 923 K (or 1098 K) for 3 h to give samples designated WZ923 (or WZ1098). Fe- and Mn-containing catalysts were prepared by incipient wetness impregnation of the dried (or, alternatively, dried and calcined) WZ with solutions of first $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and then $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in water, with drying at 383 K after each impregnation and calcination at 923 (Sample FMWZ923). The catalysts are listed in Table 1.

BET surface areas of the catalysts were measured with a Carlo Erba Sorptomatic 1800 after drying at 473 K in dynamic vacuum for 1 h. Raman spectra were recorded as before (14); the laser power at the sample was approximately 30 mW. Catalytic reactions were conducted in a once-through plug flow reactor at 1.00 bar (14, 15). The reaction temperature was 523 K; the partial pressure of

n-pentane was 0.01 bar; N_2 was a diluent. The feed flow rate was 20 ml (NTP)/min; the catalyst mass was 1.0 g. Hydrocarbon products were analyzed by on-line gas chromatography (12). Before each reaction experiment, the catalyst was pretreated in flowing air (or N_2) [30 ml (NTP)/min], heated (10 K/min) from 25 to 673 K, held at 673 K for 1 h, and cooled to 523 K (reaction temperature) in flowing N_2 (30 ml (NTP)/min) for 30 min.

Normalized conversion to a product (containing *i* carbon atoms) is defined as (mol of product formed/mol of *n*-pentane fed) · (*i*/5). The selectivity to a product containing *i* carbon atoms is the normalized conversion to the product/*n*-pentane conversion. Because the conversions were less than a few percent, they were assumed to be differential and used to calculate rates; the rate of product formation was estimated as (normalized conversion to product) · (mol of *n*-pentane fed)/(s · g of catalyst).

Figure 1 shows rates of *n*-pentane conversion per unit surface area of catalyst at 523 K as a function of time on stream (TOS) for Sample FMWZ923 (curve a) and Sample WZ923 (curves b and c). The corresponding selectivities are shown in Figs. 2A and 2B, respectively. The sample without Fe and Mn is characterized by selectivities for formation of the major product 2-methylbutane (isopentane), which were initially about 53% and increased to about 65% during the first 3 h on stream. Sample FMWZ923 is characterized by selectivities for isopentane that were initially much lower (40%) but increased within the first 2 h on stream to about 70% (Fig. 2B); other products were isobutane, propane, and traces of hexanes and *n*-butane. Qualitatively the same trends at significantly lower levels of activity (reduced by factors of ca. 3–5) were observed for the samples calcined at 1098 K. The rate at zero TOS was again essentially zero for unpromoted and promoted materials. The activity of Sample WZ1098, which was initially higher than that of the Sample FMWZ1098, passed through a maximum and then decreased. Sample FMWZ1098 reached stable activity after ca. 3 h on stream without passing through a maximum. The selectivities within the first 4 h on stream of Sample WZ1098 increased from 56 to 60% for isopentane and slightly

TABLE 1
Compositions and Surface Areas of Tungstated Zirconia Catalysts^a

Catalyst sample	wt% Fe	wt% Mn	Surface area (m ² /g)
WZ923	—	—	104
WZ1098	—	—	45
FMWZ1098	1.0	0.5	69
FMWZ1098	1.0	0.5	26

^a Each sample contained 19 wt% WO₃.

decreased from 33 to 27% and 14 to 10% for isobutane and propane, respectively. In contrast (and similar to Sample WZ923), the selectivity of Sample FMWZ1098 for isopentane steeply increased from 18 to 66%, while the selectivities for isobutane and propane decreased from 32 to 16% and from 51 to 18%, respectively.

The rate at zero TOS was essentially zero for each catalyst (Fig. 1), increasing with TOS and passing through a clear maximum when the catalyst lacked Fe and Mn. The occurrence of an induction period (arbitrarily defined as that preceding the maximum in activity) suggests the formation of reactive carbonaceous deposits or catalytic sites during operation (7, 16). The catalyst containing Fe and Mn had a nearly constant activity after the induction period of approximately 4 h TOS, whereas the catalyst without Fe and Mn deactivated rapidly after the induction period, consistent with reported results (7). The selectivities changed during the induction periods (Fig. 2).

A change in the pretreatment atmosphere (N₂ or air) had essentially no effect on the catalytic performance of Sample WZ923, and the data following the induction period show continuing deactivation of this catalyst for 10 h on stream (Fig. 1). In contrast, the catalyst with Fe and Mn

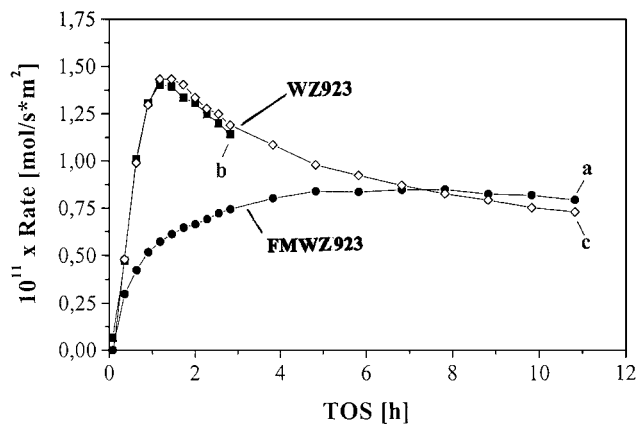


FIG. 1. Rate of *n*-pentane conversion as function of time on stream in a flow reactor at 523 K. Catalyst samples (a) FMWZ923 and (b and c) WZ923. Closed symbols represent catalysts pretreated in air; open symbols represent those pretreated in N₂.

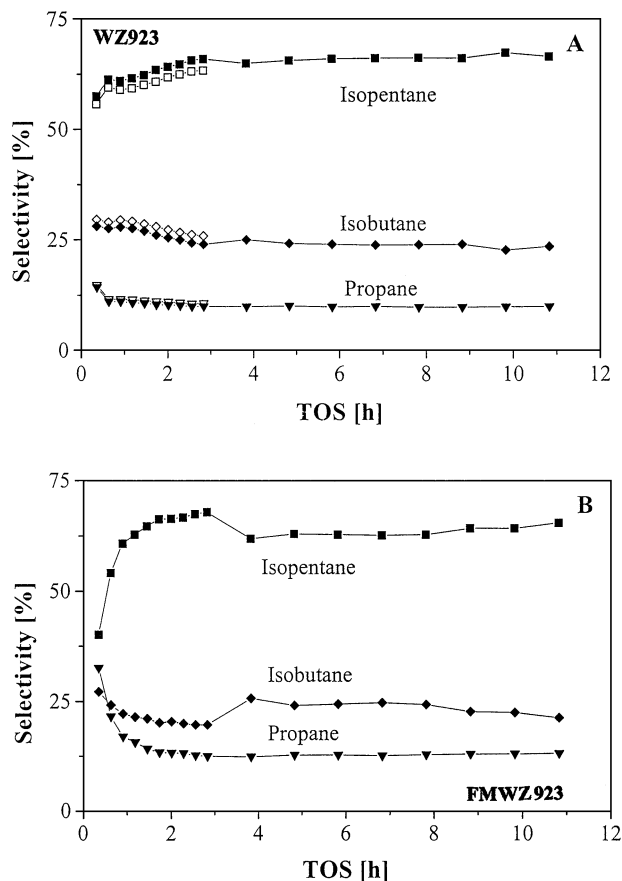


FIG. 2. Selectivity data characterizing *n*-pentane conversion as function of time on stream in a flow reactor at 523 K. (A) Catalyst sample WZ923; (B) catalyst sample FMWZ923.

(FMWZ923) showed an increasing activity and then a period of near steady-state activity for up to 11 h on stream (when the experiment was stopped, Fig. 1). Thus, the results show that the addition of Fe and Mn to WZ barely affects the activity of the catalyst after several hours on stream, when stationary activity has been achieved. The promoter roles of Fe and Mn in SZ do not pertain to WZ, although the preparation procedures were comparable for the two catalyst types (15).

The significant difference in the performance of the two catalysts shows up in the first few hours of operation, when the catalyst without Fe and Mn increases rapidly in activity followed by a decline and that with Fe and Mn increases gradually to a nearly constant activity (Fig. 1). The behavior of the former catalyst is qualitatively similar to that of sulfated zirconia and Fe- and Mn-promoted sulfated zirconia. The Fe and Mn in the tungstated catalyst apparently suppress some reactivity that is associated with an initial rapid increase in the *n*-pentane isomerization rate. We suggest that the zirconia support may play a role in WZ comparable to that of a redox initiator role attributed to Fe and Mn in FMSZ (17); this role of the zirconia may be

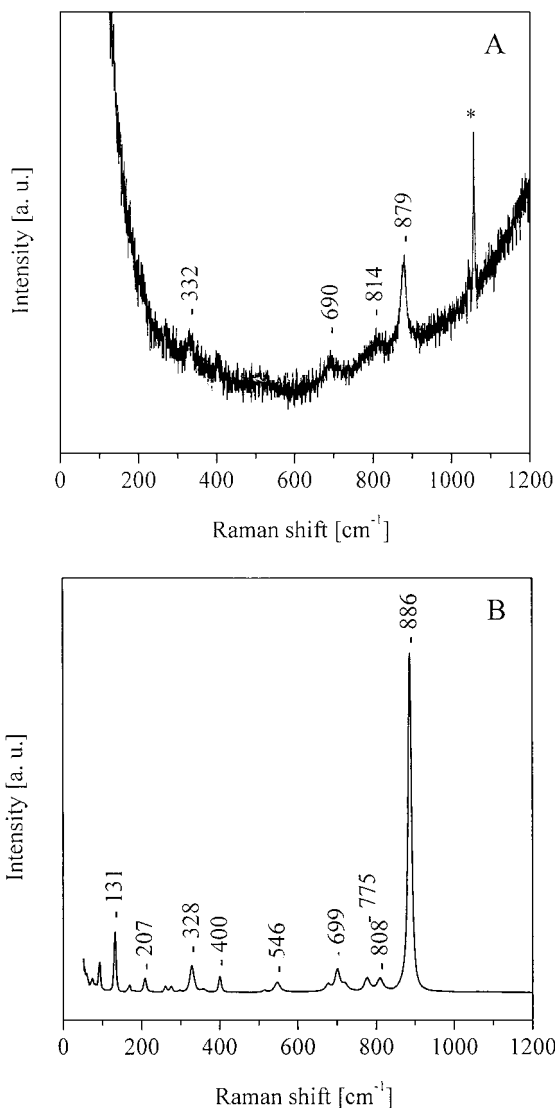


FIG. 3. Raman spectra: (A), FeWO_4 and (B), MnWO_4 . The symbol * indicates plasma lines of the laser.

suppressed in FMWZ because the zirconia is largely covered with tungstates.

The Raman spectra provide evidence that is consistent with the formation of tungstates of Fe and Mn. The Raman spectra of the pure tungstates (16, 18) are shown in Fig. 3. FeWO_4 is characterized by a noisy spectrum exhibiting one sharp band of moderate intensity at 879 cm^{-1} ; MnWO_4 is characterized by a strong sharp band at 886 cm^{-1} . The Raman spectra of the catalyst WZ calcined at 923 K include bands (not shown) of tetragonal ZrO_2 (at $148, 290, 311, 454,$ and 647 cm^{-1}) and the typical feature of the hydrated WO_x layer in the high-frequency region between ca. 825 and 993 cm^{-1} (5) (Fig. 4A). No additional bands were observed at wavenumbers below ca. 720 cm^{-1} in the spectra of the Mn- and Fe-containing samples (not shown), and the characteristic bands of polycrystalline WO_3 at $274, 715,$

and 807 cm^{-1} are absent (Fig. 4A, spectrum b). However, new weak bands or shoulders were detected in the high-frequency region at ca. $717, 860,$ and 886 cm^{-1} for Sample FMWZ923 (data not shown). These observations suggest the presence of manganese and iron tungstates in the catalyst. The broadness of the weak bands could be an indication of more-or-less amorphous iron and manganese tungstate phases.

The band at 886 cm^{-1} becomes much more pronounced after calcination at higher temperature, as in Sample FMWZ1098; in the spectra of Samples WZ1098 and FMWZ1098 the bands of microcrystalline WO_3 at $274, 715,$ and 807 cm^{-1} (not shown) are the strongest; those characterizing the WO_x overlayers are also detectable (Fig. 4B). Microcrystalline WO_3 forms in these materials because they sinter at the high calcination temperature (Table 1), and hence the WO_3 loading is beyond surface saturation. The estimated saturation coverage is ca. $10\text{ wt}\%$ WO_3 for WZ calcined at 1098 K (5). The band at 886 cm^{-1} is now clearly evident in the spectrum of the catalyst containing Fe and

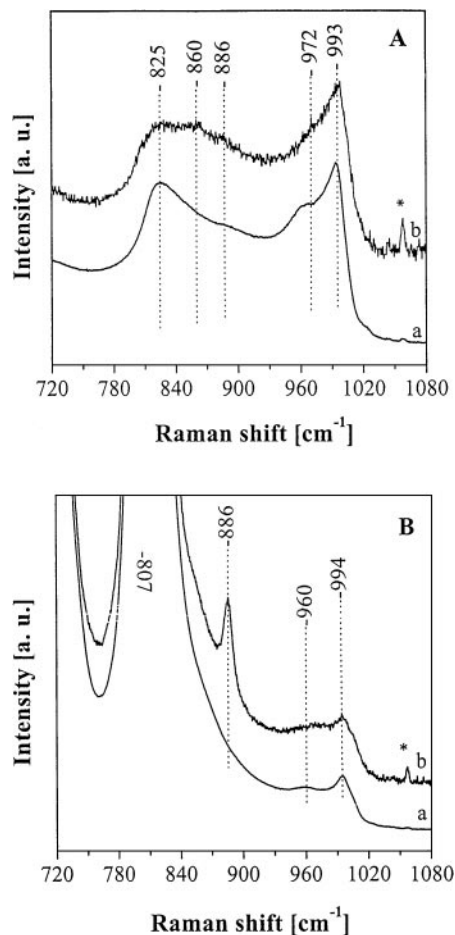


FIG. 4. Raman spectra of catalysts. (A) Sample WZ923 (a) and Sample FMWZ923 (b) in their hydrated state. (B) Sample WZ1098 (a) and sample FMWZ1098 in the hydrated state. The symbol * indicates plasma lines of the laser.

Mn (Fig. 4B, spectrum b). By comparison with the reference spectrum of MnWO_4 (Fig. 3), which has a strong band at 886 cm^{-1} , we attribute this band to microcrystalline MnWO_4 . Although a characteristic Raman band at 223 cm^{-1} indicating microcrystalline Fe_2O_3 was observed in the spectra of FMSZ (14), it is not detectable in the spectra of FMWZ.

WO_x species on ZrO_2 supports give rise to Raman bands at 960 and 994 cm^{-1} in the high-frequency regime (Fig. 4). The distinct band at 994 cm^{-1} becomes detectable only at loadings near or beyond saturation (5). These results suggest that some of the WO_x species on Samples WZ923 and WZ1098 reacted with Mn-containing (and possibly Fe-containing) precursor(s) to give MnWO_4 (and possibly iron tungstate) during the preparation. Thus, in summary, we infer that because of the formation of the manganese (and possibly iron) tungstate, the Fe_2O_3 clusters and dispersed Mn^{2+} species present in FMSZ (14) cannot be formed and that therefore these components cannot exert their promoter effect in the steady-state catalytic regime (Fig. 1); furthermore, coverage of the zirconia with the tungstates may suppress an initiator role manifested by the performance of WZ during the induction period.

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