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SUPPORTING INFORMATION

Synthesis of isomorphically substituted Ru manganese molecular sieves and their catalytic properties for selective alcohol oxidation

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1. Catalyst Characterization

1.1 Chemical composition by ICP-AES and XEDS techniques and surface area measurements:

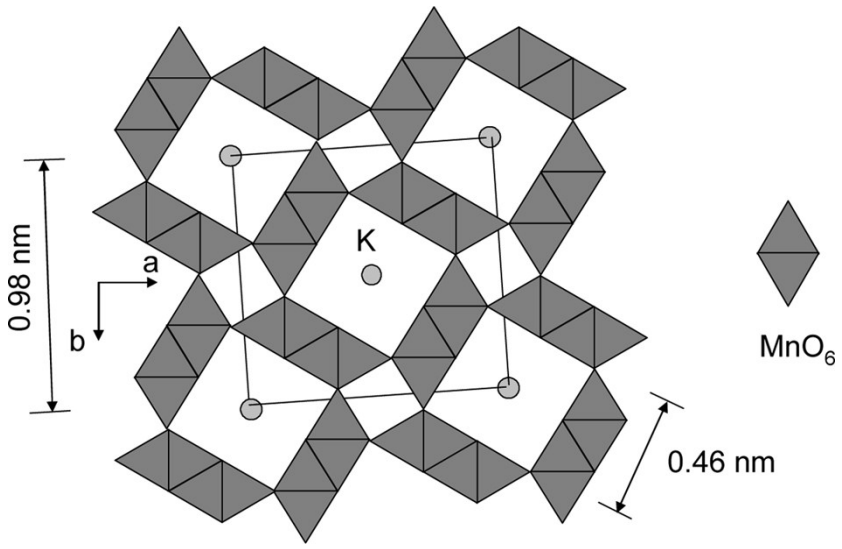


Figure S1: Scheme of the cryptomelane type molecular sieve.

Extracted from: Y. – S. Ding, X.-F. Shen, S. Sithambaram, S. Gomez, R. Kumar, V.M.B. Crisostomo, S.L. Suib, M. Aindow; *Chem. Mater.*, **2005**, *17 (21)*, 5382–5389

Table S1a: Chemical composition of [Ru]-K-OMS2 (2 wt%) and K-OMS2 obtained by ICP-AES and XEDS techniques.

	[Ru]-K-OMS2 (2 wt%)		K-OMS2
Wt (%)	**ICP-AES**	**XEDS**	**ICP-AES**
Ru	2.0	2.3	-
K	4.8	3.8	4.9
Mn	55.6	57.8	61.4

Table S1b: Metal content of catalysts included in Table 2

Entry	Catalyst	% wt metal (ICP-AES)
1	RuO_x/K-OMS2(1wt%)	0.98
2	RuO_x/K-OMS2(2wt%)	2.2
3	Cu/MnO_x(3wt%)	3.0
4	Cu/Mn_2O_3(3wt%)	3.0
5	RuO_x/Al_2O_3(1wt%)	0.98
6	RuO_x/ZrO_2(1wt%)	1.02
7	RuO_x/TiO_2(1wt%)	0.93

Table S2: Surface area of [Ru] – K – OMS2 (2 wt %) and K – OMS2[a].

Area BET (m^2/g)	Before reaction	After reaction
K-OMS-2	52.2	27.8
[Ru] – K – OMS2 (2 wt%)	131.1	48.8

[a] Measured using CO_2 (273K) as adsorbent gas (fitting according to the Dubinin-Radushkevich equation) [ref: L. Yun, Q. Zhang, J. Garcia-Martinez, S. L. Suib, J. Am. Chem. Soc., 2008, 130, 3198-3207; Y.H. Hu, E. Ruckenstein, Chem. Phys. Chem., 2006, 425, 306-310]

1.2 HAADF-STEM with energy dispersive X ray (XEDS) (mapping of K, Mn and Ru elements).

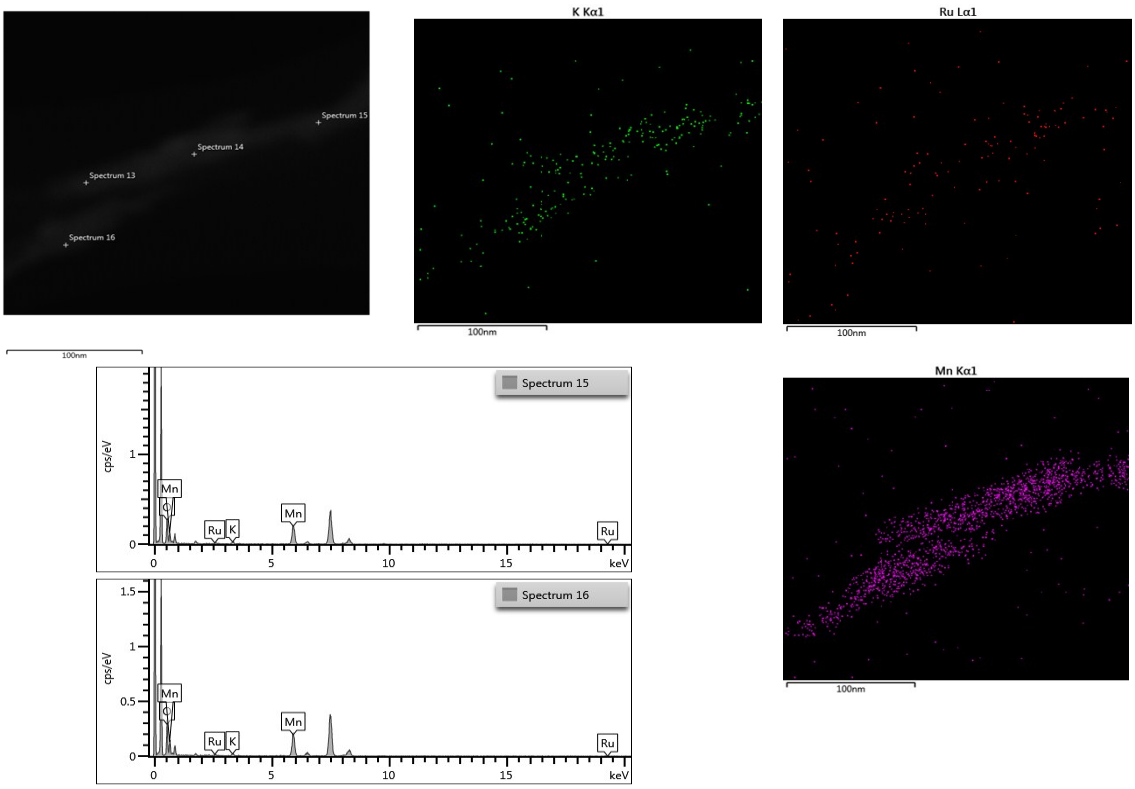
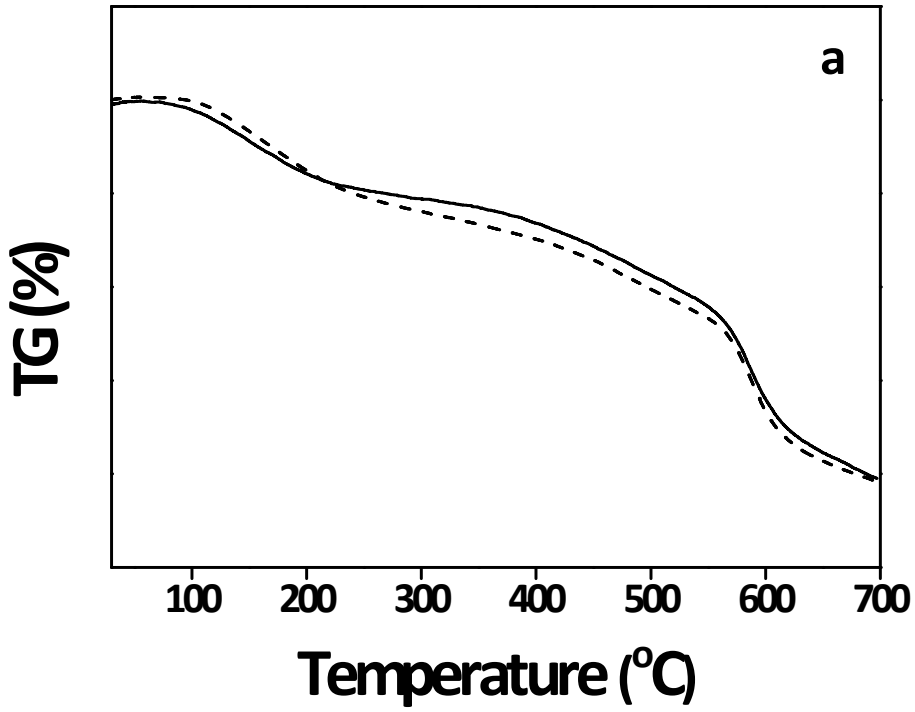
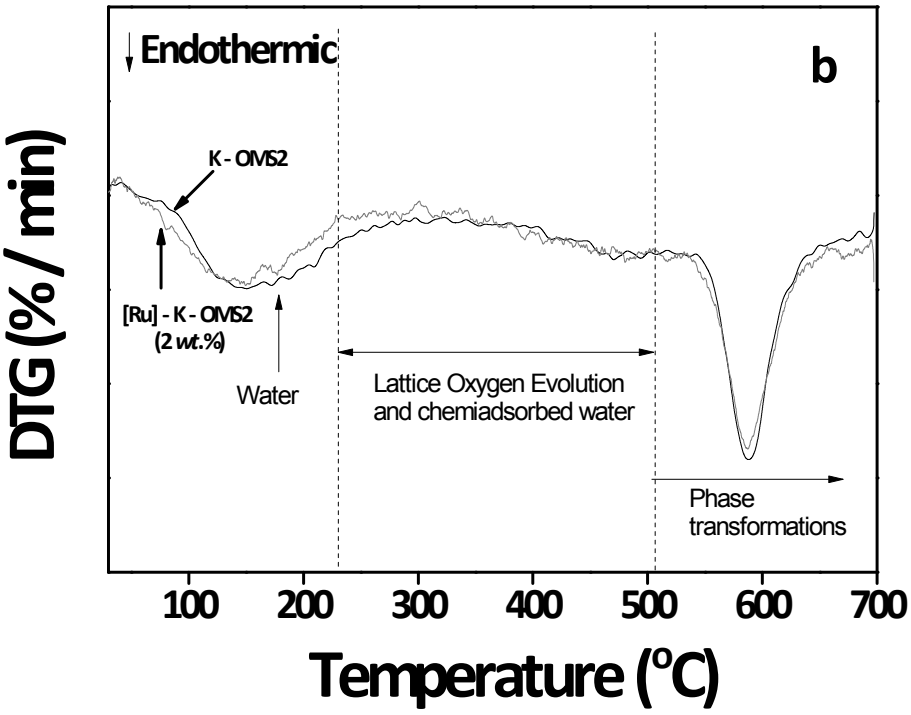


Figure S2 Mapping of K, Mn and Ru elements by using HAADF-STEM with energy dispersive X ray (XEDS) of [Ru]-K-OMS2 (2 wt%).

1.3 Thermogravimetric studies: TGA and DTG analysis





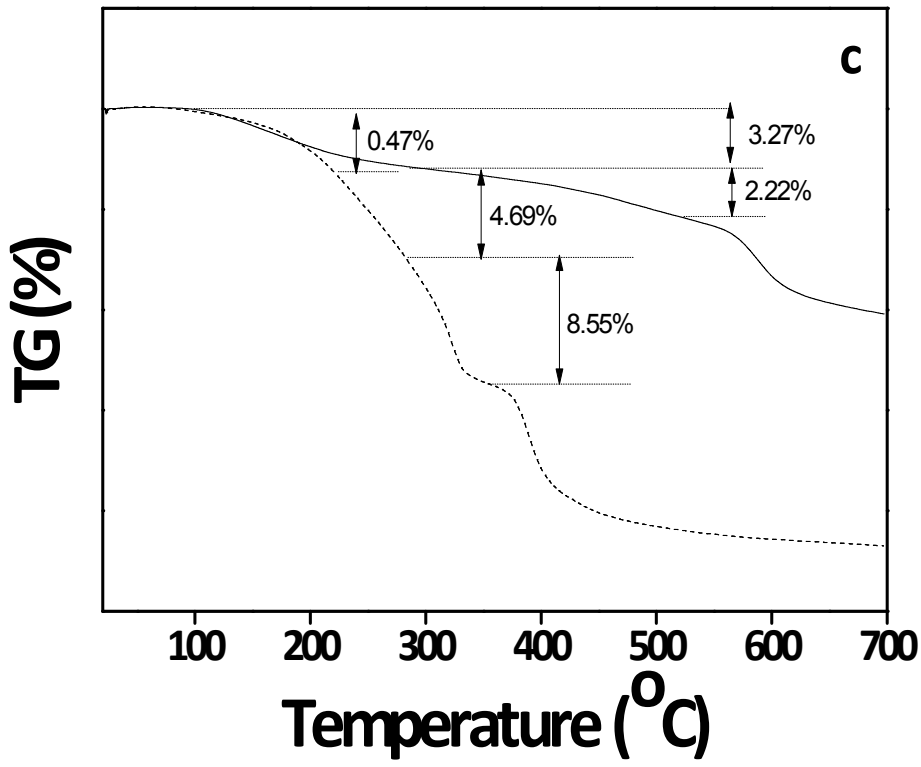


Figure S3: a) Thermogravimetric analysis for K-OMS2 (solid line) and [Ru] (2% *wt*)– K – OMS2 (dashed line); b) DTG analysis for K-OMS2 (black) and [Ru]-K-OMS2 (2 wt%) (grey), c) Thermogravimetric analysis for [Ru]-K-OMS2 (2 wt%): before reaction (solid line) and after reaction (dashed line)

1.4. UV spectroscopy

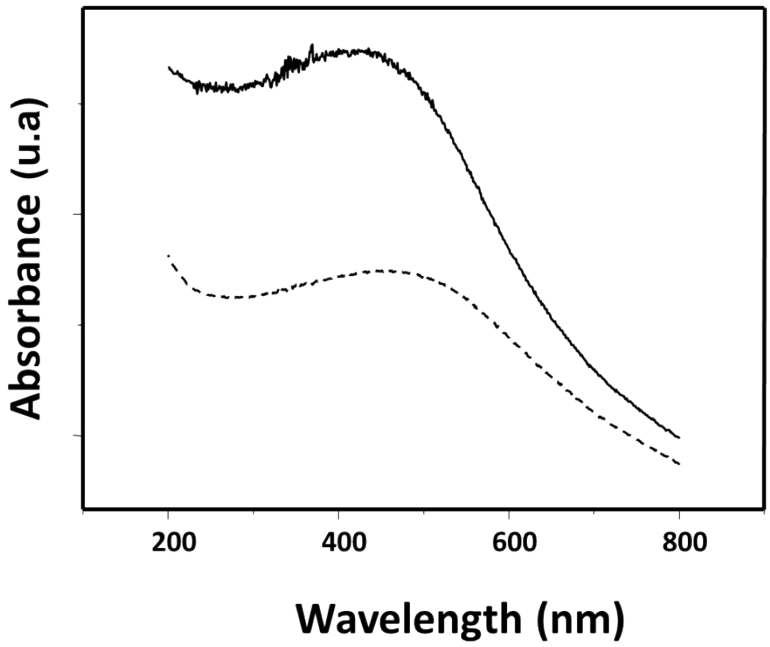


Figure S4: UV-Vis spectra of the K-OMS2 (dashed line) and [Ru]-K-OMS2 (2 wt%) (solid line).

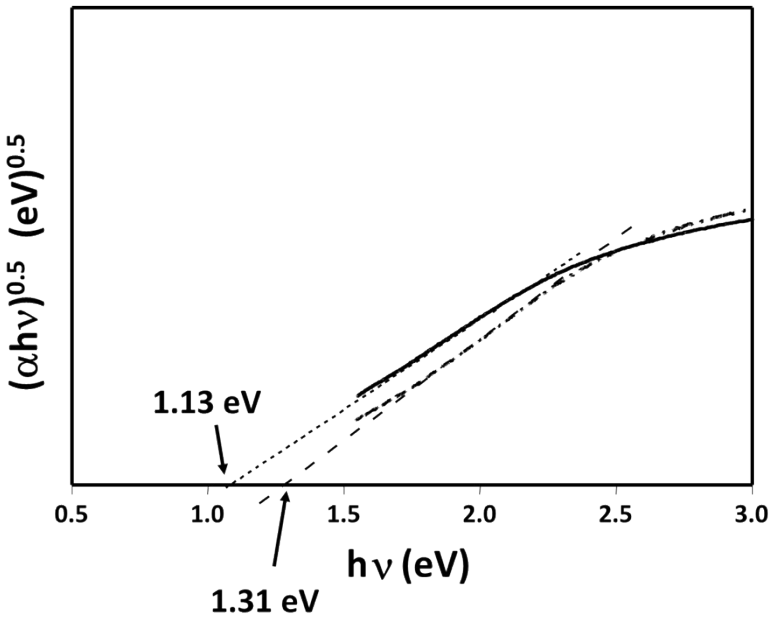


Figure S5: Estimation of the band gap (in eV) for K-OMS-2 (dashed line) and [Ru]-K-OMS2 (2 wt%) catalyst (solid line).

2. Catalytic studies

2.1. Comparative kinetics of the oxidation of benzyl alcohol to benzaldehyde with catalysts included in Table 2.

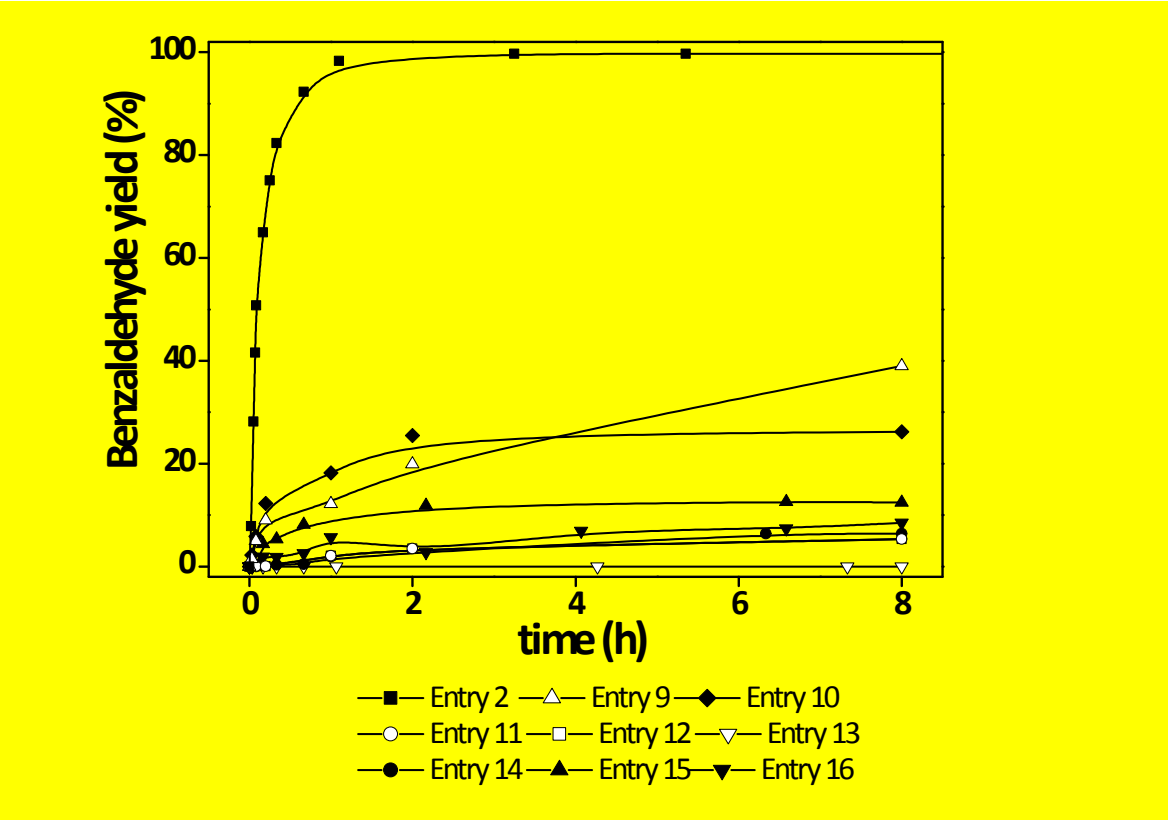


Figure S6: Evolution of benzaldehyde yield with time in the presence of catalysts included in Table 2.

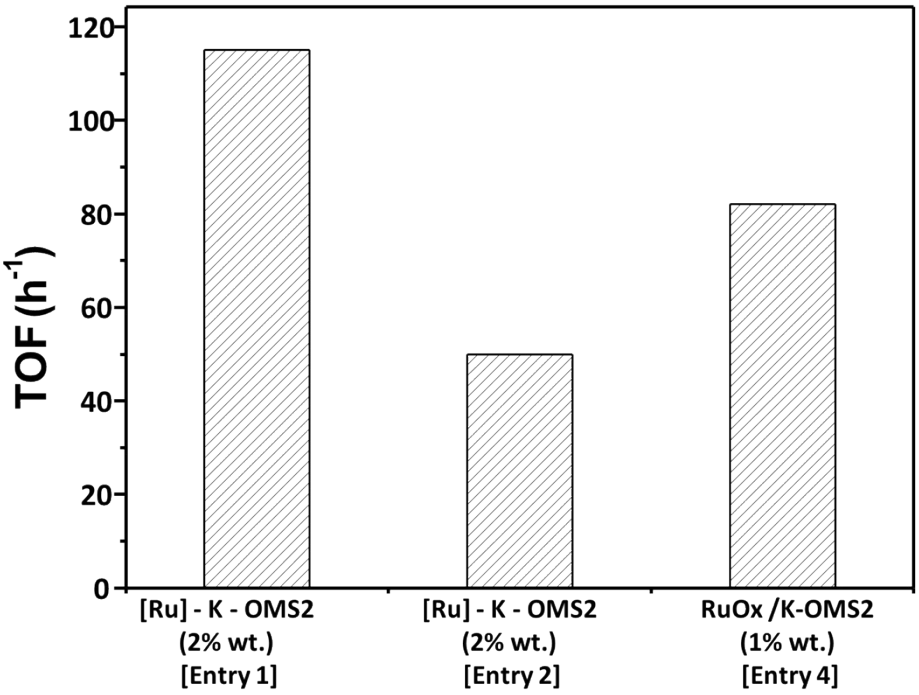


Figure S7: TOF values obtained for the Ru- doped catalysts (entries 1, 2 and 4 in Table 2).

2.2. Comparative kinetics of the oxidation of benzyl alcohol to benzaldehyde with catalysts K-OMS2, [Ru]-K-OMS2 (2 wt%) and RuO_x (1 wt%)-K-OMS2 under inert atmosphere.

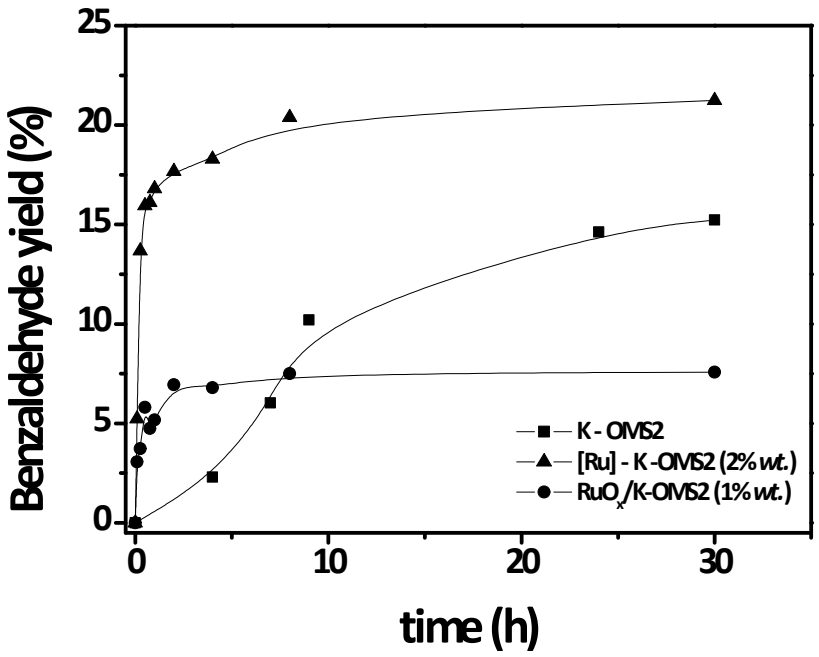


Figure S8: Evolution of benzaldehyde yield with time under inert atmosphere in the presence of [Ru]-K-OMS2 (2 wt%), RuO_x/K-OMS2 (1 wt%) and K-OMS2 as a catalyst. (entries 3, 5 and 8 in Table 2).

2.3. Leaching studies

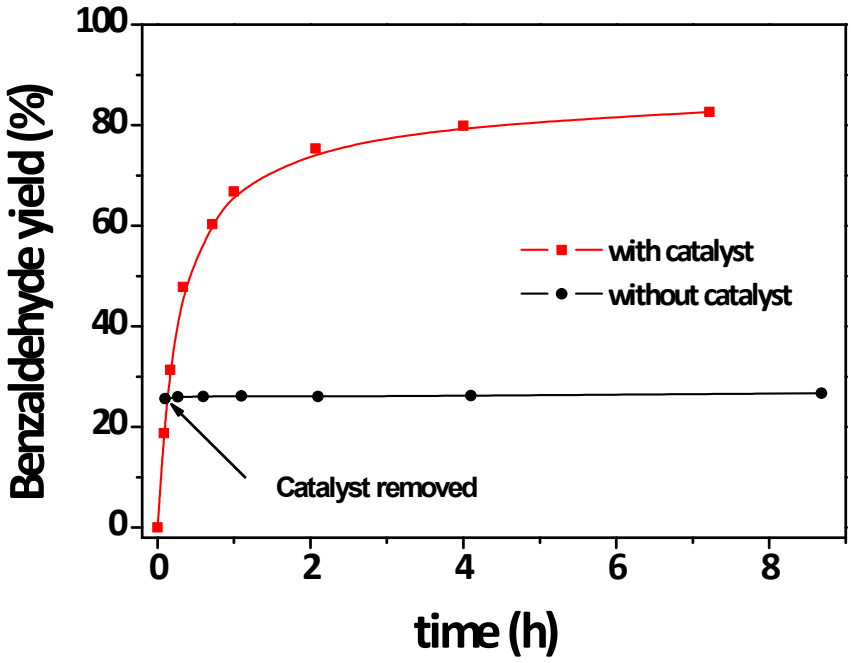


Figure S9: Graphics representing the evolution of benzaldehyde yield (%) with time when the solid [Ru]-K-OMS2 (2 wt%) is separated by hot filtration. The arrow shows the point when filtration is used to separate the solid.

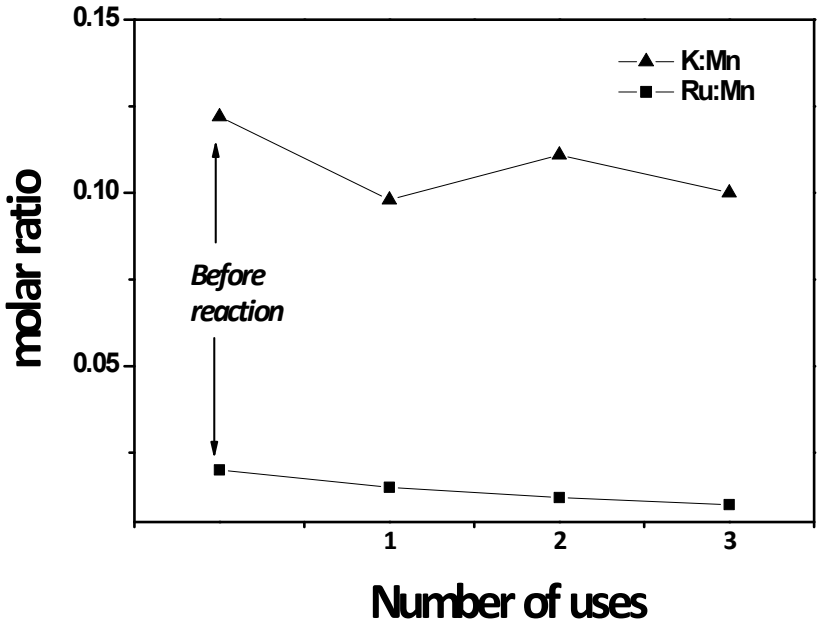
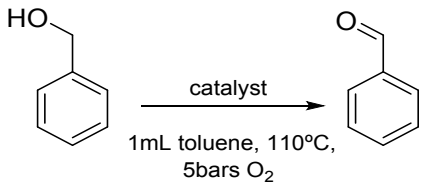


Figure S10 Graphics representing the variation of the K/Mn and Ru/Mn content obtained by ICP analysis with number of uses for [Ru]-K-OMS2 (2 wt%) during the oxidation of benzyl alcohol to benzaldehyde.

3. Mechanistic Studies

3.1 Influence of additives

Table S3: Study on the influence of products in the performance of the catalyst [Ru]-K-OMS2 (2 wt%) during the oxidation of benzyl alcohol to benzaldehyde[a].



Entry	Additive[b]	Amount (mmol)	Conversion(%)	Selectivity(%)
1	----	---	83	100
2	H_2O	0.6	69	100
3	benzaldehyde	0.1	16	100
4	benzaldehyde + H_2O	0.1 + 0.6 respectively	17	100
5	benzoic acid	0.1	50	100

[a]: Experimental conditions: benzyl alcohol (0,25 mmol), catalyst (0.5mmol% Ru), toluene (1ml), n-dodecane (internal standard), T = 110ºC, P_{O2} = 5 bar; [b]Experiments carried out under the same experimental conditions described in [a] and the added mass of water and/or benzaldehyde represents a conversion of 40%.

4. Regeneration and reuse studies.

4.1 Catalytic studies after different uses

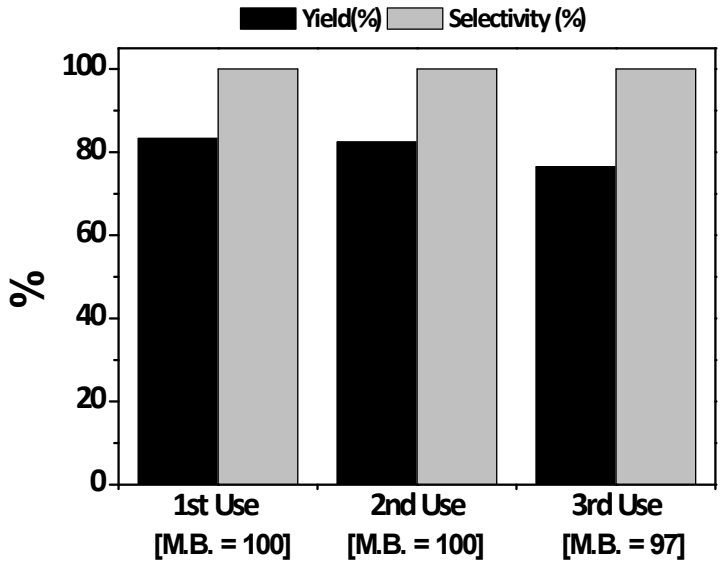


Figure S11. Studies on recovery and reuse of [Ru]-K - OMS2 (2 wt%) catalyst. (M.B: indicates mass balance (%).

4.2 DRX diagrams after different uses:

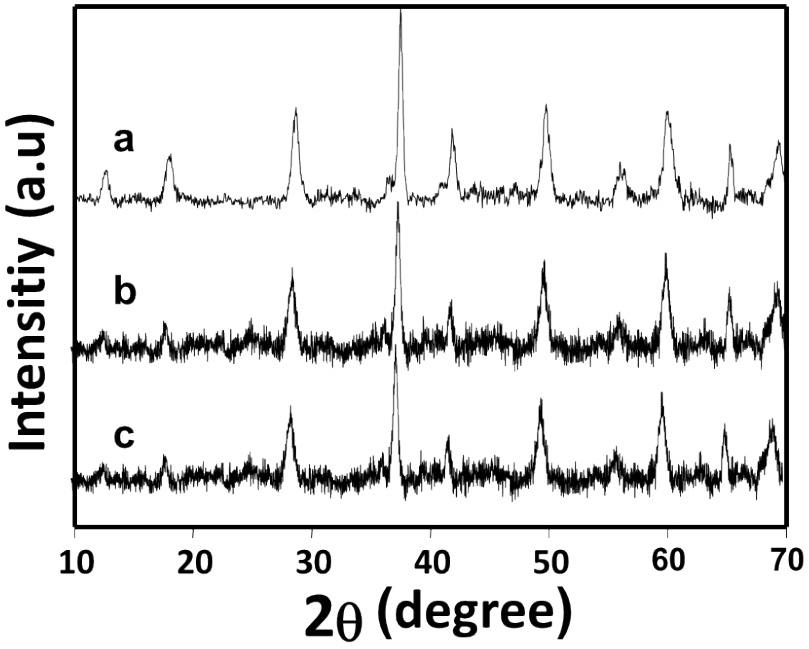


Figure S12. DRX diagrams of [Ru]-K - OMS2 (2 wt%) after the uses: a) 1st use b) 2nd use and 3) 3rd use.